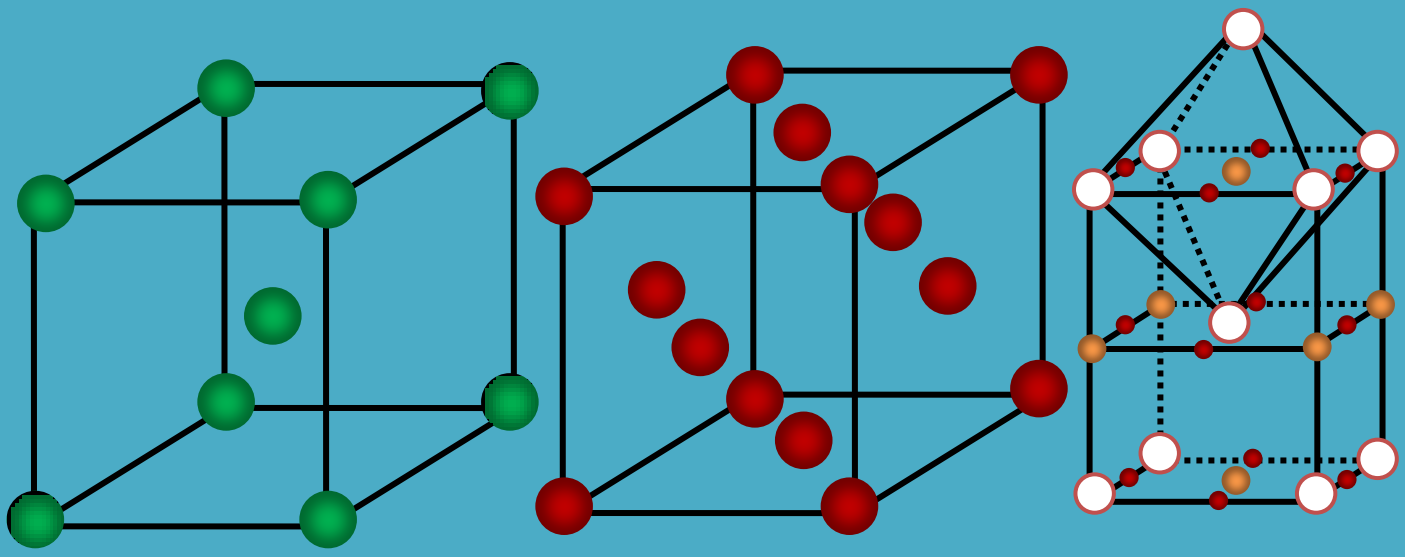
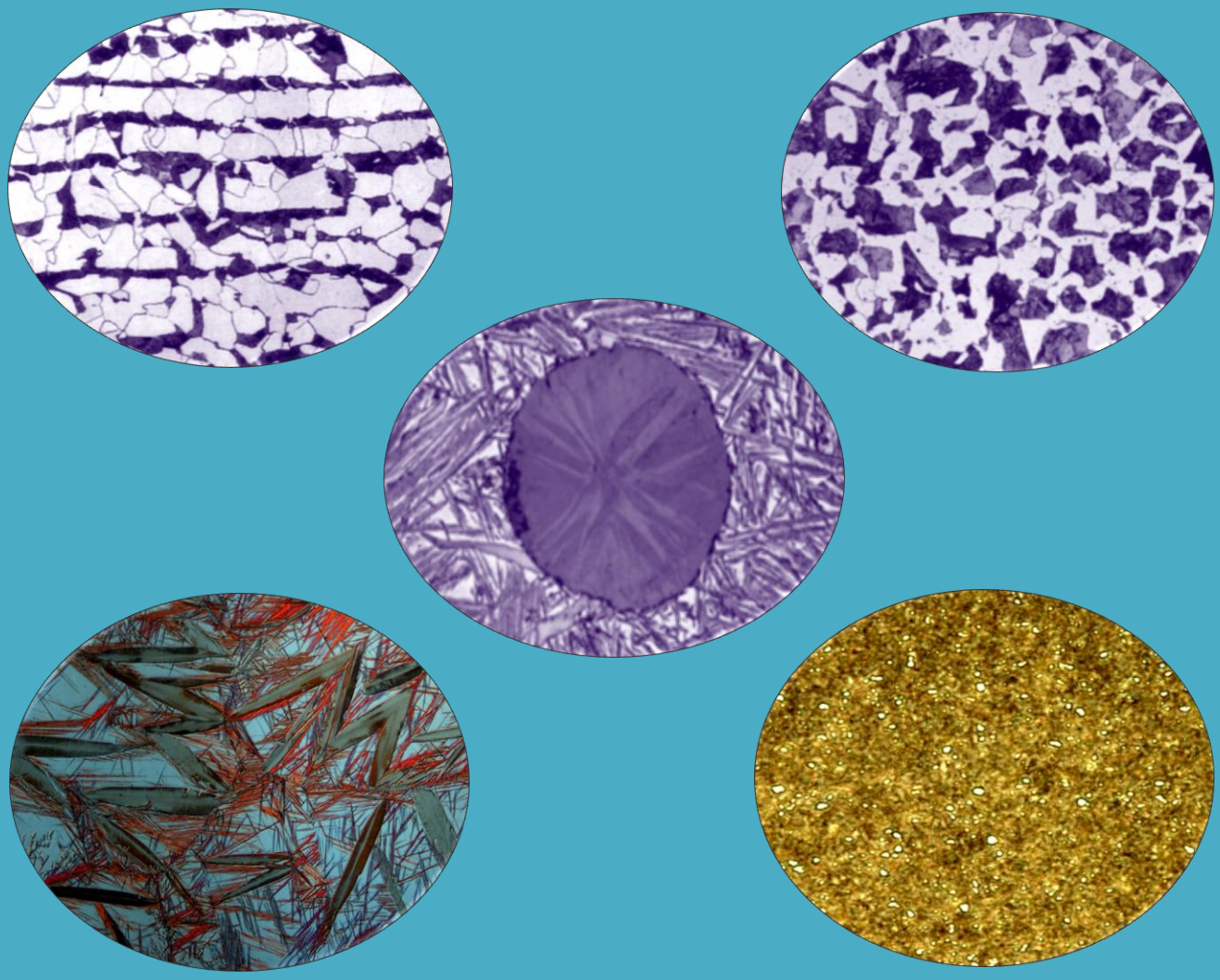


# Heat Treatment of Metallic Alloys

Md. Aminul Islam



# Chapter One

## Physical Metallurgy and Heat Treatment of Steels

### 1.1 Introduction

Heat treatment may be defined as heating and cooling operations applied to metals and alloys in solid state so as to obtain the desired properties. Sometimes, heat treatment is done inadvertently due to manufacturing processes that either heat or cool the metal such as welding or forming. In heat treatment operations, the heating and cooling cycles or the sequence of two or more such operations applied to steels in order to modify its metallurgical structure. This is done in such a way that the targeted physical, mechanical and chemical properties are incorporated. Usually, it consists of heating the steels to some specific temperatures, holding at these temperatures for a predertmined time periods and cooling to room temperature or below the room temperature with a definite rate, Fig.1.1.

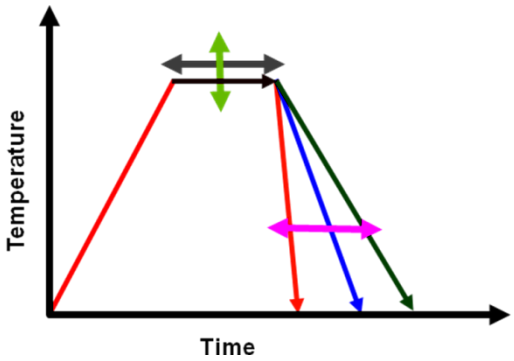



Figure 1.1: Schematic diagram showing the heat treatment cycle.

Heat treatment is often associated with increasing the strength of material, but it can also be used to soften the matrix, refine the grain size, relieve internal stress, improve machinability and formability and restore ductility after a cold working process. Some basic objectives of heat treatment of steels are summarized as follows:

a) Improvement in ductility
b) Relieving internal stresses
c) Refinement of grain size
d) Increasing hardness or tensile strength
e) Improvement in machinability
f) Alteration in magnetic properties
g) Modification of electrical conductivity
h) Improvement in toughness
i) Increase in corrosion resistance, etc.

## 1.2 Heat Treatment of Steels

A steel is usually defined as an alloy of iron and carbon with the carbon content between a very small amount to about 2.0 wt%. Other alloying elements can amount in total to about 8wt% in low alloy steels, which is much higher in the case of highly alloyed steels such as tool steels and stainless steels. On the other hand, for microalloy steels, the total amount of alloying elements will be not more than 0.5%. Since iron is the basic element of steel, knowledge on some of its properties is a prerequisite to an understanding of the fundamental principles underlying the heat treatment of steels.

Some chemical elements can stay in two or more forms of physical conditions, which may differ in the arrangement of atoms in crystalline solids or in the occurrence of molecules that contain different numbers of atoms. These elements are said to be allotropic. Iron is an allotropic material. If molten sample of pure iron was allowed to cool slowly and the temperature of the iron was measured at regular intervals, an idealized (equilibrium) time temperature plot of the data would appear as shown in Fig.1.2.

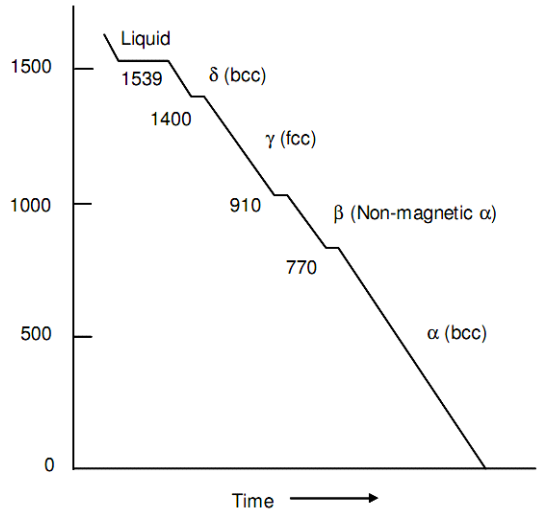



Figure 1.2: Allotropic behaviours of pure iron.

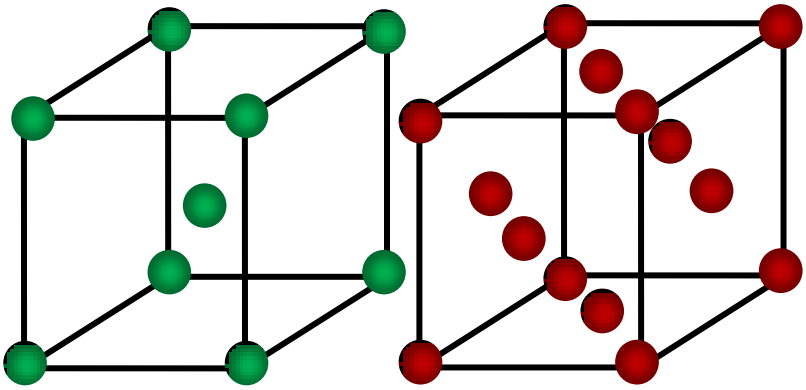


Figure 1.3: BCC and FCC cells of iron.

The discontinuities (temperature arrests) in this curve are caused by physical changes in the iron. The first arrest at 1539°C marks the temperature at which the iron freezes. The other arrests (known as transformation temperatures or critical points) mark temperatures at which certain internal changes take place in the solid iron. Some of these temperatures are very important in the heat treatment of steel. The atoms in all solid metals are arranged in some definite geometric (or crystallographic) pattern. The atoms in iron, immediately after freezing, are arranged in what is termed the body centered cubic (BCC) system. In this crystal structure the unit cell consists of a cube with an iron atom at each of the eight corners and another in the center (Fig.1.3). Each of the individual grain (crystal) that composes the solid metal is built up of a very large number of

these unit cells, all oriented alike in the same grain. This high temperature form of iron is known as delta (δ) iron.

At 1400°C, iron undergoes an allotropic transformation, that is, the arrangement of the atoms in the crystal changes. The new crystal structure is face centered cubic (FCC) and the unit cell again consists of a cube with an iron atom at each of the; eight corners, but with an iron atom in the center of each of the six faces instead of one in the center of the cube like BCC. This form is known as gamma (γ) iron. At 910°C iron undergoes another allotropic transformation and reverts to the body centered cubic system. This structure, which is crystallographically the same as delta iron, is stable at all temperatures below 910°C and is known as alpha (α) iron. The arrest at this temperature is due to nonmagnetic alpha to magnetic alpha. It marks the temperature at which iron becomes ferromagnetic and is, therefore, termed the magnetic transition. Above this temperature iron is nonmagnetic. These various temperature arrests on cooling are caused by evolutions of heat. On heating, the arrests occur in reverse order and are caused by absorption of heat.

### 1.3 Mechanical Properties

Iron is relatively soft, weak and ductile and cannot be appreciably hardened by heat treatment. Its tensile strength at room temperature is around 20,000 lb/in$^2$, yield strength is well below of the tensile strength, Brinell hardness is about 80 and the modulus of elasticity is about 29,000,000 lb/in$^2$ ( Fig.1.4).

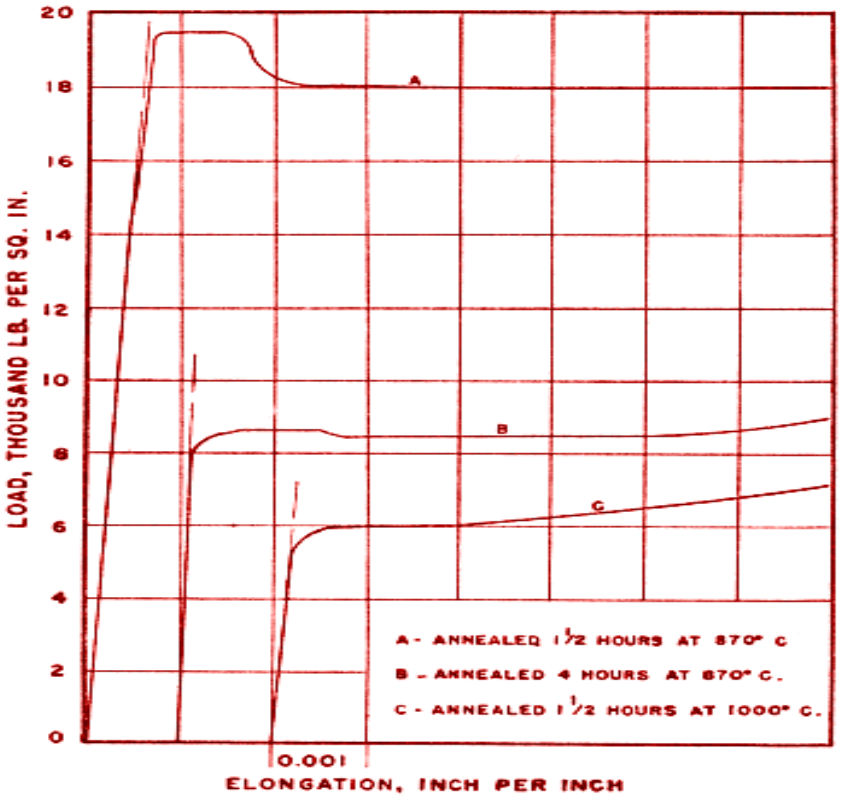



Figure 1.4: Tensile behaviour of pure iron.

On the other hand, the tensile strength significantly decreases with increase in heating temperature or time above the critical temperature, Fig.1.4. However, cold working can cause ferrite grains to be deformed and curled (Fig.1.5) that increase the tensile strength and hardness of the pure iron with corresponding decrease in ductility, by cold working.

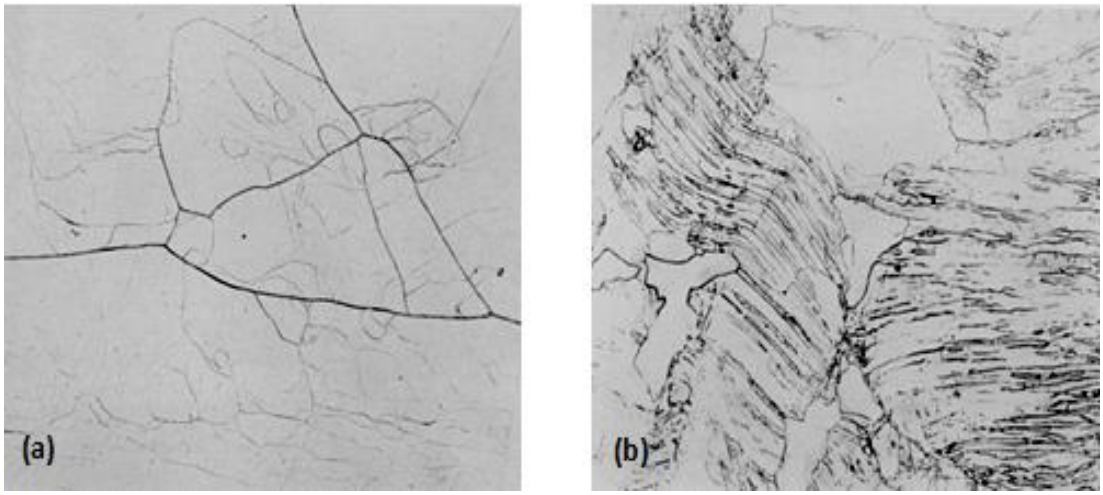



Figure 1.5: Microstructures of pure iron (a) before cold working and (b) after cold working.

We know that steel is an alloy of iron and carbon and with increase in carbon content the strength of the steel is changed significantly. Through the change in heat treatment parameters, for a fixed carbon as well as residual elements, the mechanical, physical and chemical properties of steels can be changed to a wide scale. Although plain carbon steels have some appreciable properties, it also contains some limitations. These are:

a) They cannot be strengthened beyond about 100000 psi without significant loss in toughness (impact resistance) and ductility.
b) Large sections cannot be made with a martensite structure throughout and thus are not deep hardenable.
c) Rapid quench rates are necessary for full hardening in medium carbon content leads to shape distortion and cracking of heat treated steels.
d) Plain carbon steels have poor impact resistance at low temperatures.
e) They have poor corrosion resistance for engineering problems.
f) They also have a very poor high temperature oxidation resistance.

Most of the above problems are possible to overcome by additions of various alloying elements. So, for better understanding of heat treatment it is helpful if the effects of alloying elements on iron-carbon phase diagram, microstructures and properties of plain carbon steels are known.

Steel is an alloy, which is mainly produced from pig iron. In fact, the manufacture of steel is quite a long process as it comprises of numerous stages and one of these stages is refining. Indeed, once produced in furnace, the steel does contain quite significant amount of impurity and

thus, it requires to be refined to a certain degree. However, even after the refining process, the steel still contains small amounts of residual elements (also termed as trace elements), which have some negative influence on the properties of steel.

### 1.3.1 Effects of Residual Elements on Steel

As stated above, in general, the presence of trace elements is undesirable due to their bad effects on the steel and its properties. However, in specific purposes they are beneficial also. The descriptions of these elements as well as their drawbacks they cause on steels are given below in brief.

#### 1.3.1.1 Phosphorus

Phosphorus in steel can have beneficial as well as harmful effects. Phosphorus is one of the most potent solid solution strengtheners of ferrite, Fig.1.6. The addition of only 0.17% phosphorus increases both the yield and tensile strength of low carbon sheet steel by about 62 MPa (9 ksi), while also improving the bake hardening response and deep drawing ability. Because of these properties, rephosphorized high strength steels are widely used for cold forming applications. Phosphorus is also used as an additive in steels to improve machining characteristics and atmospheric corrosion resistance. As most texts on metallurgy emphasize, phosphorus also increases the hardenability of steel.

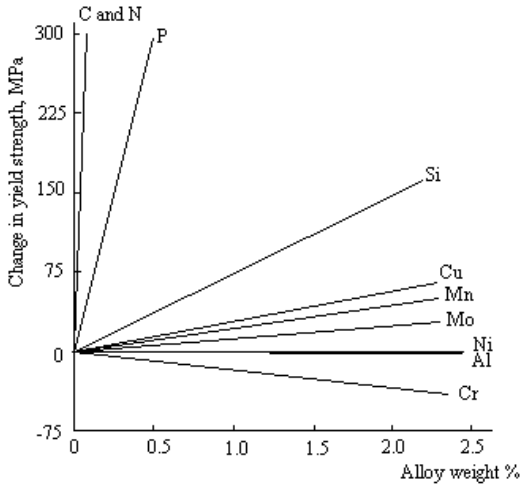



Figure 1.6: Solid solution strengthening effects of various elements in iron.

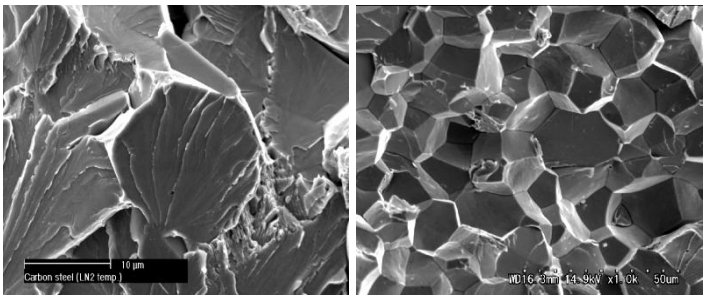


Figure 1.7: Brittle transgranular cleavage and intergranular fractures in steel.

Detrimental effects of P in steel include various forms of embrittlement, which reduce the toughness and ductility. The most familiar example in this category is the classic phenomenon of temper embrittlement in heat treated low alloy steels resulting from segregation of P and other impurities at prior austenite grain boundaries. So, the brittle fracture mode of the steel changes from transgranular cleavage to intergranular, Fig.1.7. This form of embrittlement and the contributing role of certain alloying elements has been a subject of research for several decades.

### 1.3.1.2 Silicon

Silicon increases the hardenability of the steel, but to a smaller degree, Fig.1.8. It is the same as manganese in the sense that all steel grades contains silicon along with manganese and even though it is less than manganese, it still increases the strength and hardness. The strengthening factor is due to the silicon that dissolves in the iron. It plays an important role as a deoxidizer in order to prevent defects and/or damages. Usually only small amounts (0.20%) are present in rolled steel when it is used as a deoxidizer. However, in steel castings, 0.35 to 1.00% is commonly present. Electrical steels contain a high amount of silicon as the electrical conductivity is reduced by its presence. In fact, silicon has the particularity of impairing hot and cold workability and machinability. The presence of silicon in low carbon steel is also detrimental since it affects the surface quality of the steel.

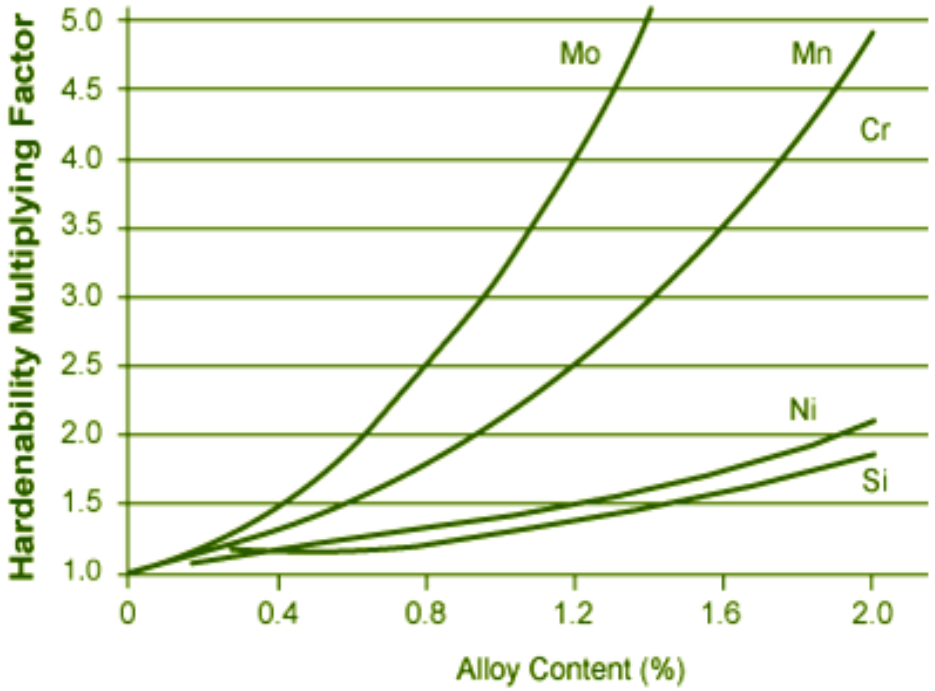



Figure 1.8: Effect of silicon content on the hardenability of steel.

### 1.3.1.3 Oxygen

Oxygen is really a poison to steel. Indeed, when present in steel, it has a very bad effect on its mechanical properties. To be more precise, oxygen reduces the impact strength of steel, whereas it also has the tendency to increase its ageing brittleness, red shortness, woody and slanty fractures, Fig.1.9. In brief oxygen reduces the toughness of steel.

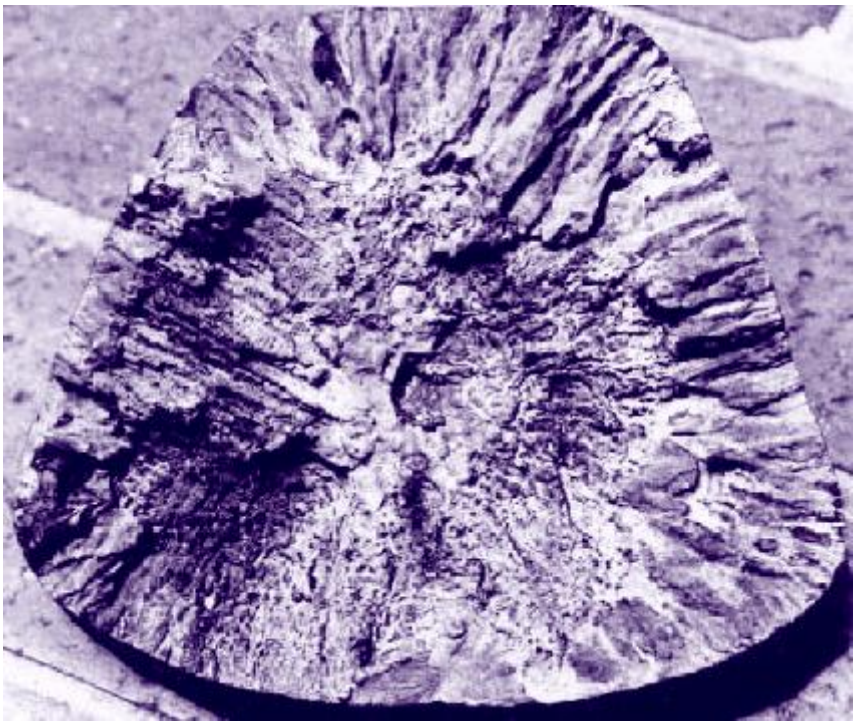


Figure 1.9: Woody and slanty fracture in metal.

### 1.3.1.4 Hydrogen

Hydrogen is an inevitable impurity in steel and cast iron. It can be quite harmful in certain applications and, where necessary, should be avoided or removed as required. The solubility of hydrogen in steel is strongly dependent on crystal structure, temperature and composition. Hydrogen is much more soluble in austenite than in ferrite. In all cases, solubility increases with temperature, ranging from less than 1 ppm at room temperature to about 8 ppm at 704$^{o}$C (1300$^{o}$F). Carbon generally increases the solubility of hydrogen, but the situation is made more complex at high temperatures by the formation of methane, $CH_4$. This element also acts as a decarburizing agent when it is in the moisted form (at high temperatures). Like Oxygen, hydrogen also is injurious to steel as it causes embrittlement by decreasing in elongation and reduction of area without any increase of yield point and tensile strength. Indeed, hydrogen is the source of redoubtable snowflake like crack formation and it favours the formation of ghost lines in the steel structure. Furthermore, atomic hydrogen engendered by pickling penetrates into the steel and forms blowholes.

### 1.3.1.5 Sulphur

Sulphur is a trace element, which has a great tendency to segregate (that is to isolate itself in the structure). It also reacts with iron to form iron sulphide, which produces red or hot shortness, since the low melting eutectic forms a network around the grains so that these hold but loosely together and the grain boundaries may easily break up during hot forming. Sulphur plays a great

role also in deteriorating the weldability, impact toughness and ductility of steel. Nonetheless, steels that are to be machined require a certain minimum sulphur content for proper chip formation. Where machining constitutes a major fraction of the end products cost, many types of steel (carbon, alloy and less often stainless) are intentionally resulphurized for just this reason.

#### 1.3.1.6 Tin

While often applied to steel as a protective and/or decorative coating or for ease of soldering, tin has never been intentionally added as an alloying agent. Even small amounts of tin are harmful to ductility and sheet formability and can cause hot shortness during forging or primary rolling. Tin is also one of the tramp elements (with phosphorus and arsenic) known to make steels susceptible to temper embrittlement, especially when chromium, nickel or manganese are also present (see Chromium). For these reasons, efforts are made to keep tin from entering the steel. Tin is not often associated with raw materials entering the blast furnace, but any tin compounds present here will be reduced, allowing tin to dissolve in the iron. A more serious problem is the carryover of tin in the scrap charge in steelmaking furnaces. Solders and tinplate are the most common sources. Some tin may also be contained in galvanizing spelters, where it is used to control spangle appearance. All such tin will be retained in the melt throughout the steelmaking process.

#### 1.3.1.7 Arsenic

Arsenic is almost always present as a trace element in steel because of its natural occurrence in iron ores, coke, ferroalloys and nonferrous addition agents. Although arsenic has a mildly beneficial effect on strength it is never intentionally added to steels, mainly because of its high toxicity. Also, even trace amounts are known to promote susceptibility to temper embrittlement, especially in chromium-nickel steels. Therefore, it is regarded as an unwanted "tramp" element.

#### 1.3.1.8 Antimony

This has as effect similar to arsenic, which also causes temper embrittlement and it affects quite considerably the toughness and the ductility of steel.

#### 1.3.1.9 Nitrogen

Nitrogen has been described as an essential, important and inexpensive alloying addition to steels, which is fortunate in that all steels contain some nitrogen. The content varies from as little as 0.002% (20 ppm) in BOF steels to about 10 times that amount in some EF steels and 150 times that amount in certain stainless grades. Nitrogen exists in steel as an interstitial quite similar to carbon and may also present as nitrides of iron, aluminum, vanadium, columbium, titanium and a number of other alloying elements. Nitrogen can be either harmful or beneficial to the steel's properties, depending on the form in which it is found. Nitrogen can also be diffused into the surface of steels to give an extremely hard case and thus used for case hardening. During heat treatment, similar to carbon, nitrogen forms an iron martensite. It has a mild but positive

effect on hardenability; it depresses the martensite-start temperature; it retards formation of proeutectoid ferrite and bainite. Nitrogen also contributes to secondary hardening in vanadium steels by affecting the precipitation of V(C,N) during tempering and, in Cr-V steels, by retaining a finer grain size during tempering due to the presence of alloy nitride particles. All steels can be nitrided but the process works best if at least one percent of alloy nitride formers, typically chromium and aluminum, are present to help produce a fine grain size. As an interstitial solid solution strengthener, nitrogen provides an inexpensive means to increase strength in hot rolled steels for automotive applications. About 0.10-0.15% N raises the yield strength of mild steels to 276-345 MPa (40-50 ksi). Cold forming and intentional strain aging in paint curing oven temperatures, for example, can further raise strengths to 414-483 MPa (60-70 ksi). Nitrogen is most widely used as a microalloying element in high strength low alloy (HSLA) steels, where it contributes to grain refinement as well as precipitation hardening. Nitrogen is also used to extend the passive range of austenitic stainless steels. Certain grades of steel, such as the Nitralloy family, were specifically designed for surface hardening treatments. Many AISI/SAE alloy steels containing Cr, Mo, V, etc., as well as die steels contain nitrogen both for strengthening and because nitrogen is an austenite stabilizer. This permits the formulation of compositions with somewhat reduced nickel contents.

**1.4 Alloy Steel**

The properties of carbon steel can be enhanced by using the appropriate alloying elements. An alloy is a mixture of two or more metals, or a metal and some other materials. Most alloy contain a large amount of one metal, called the base metal and smaller amounts of one or more other metals or nonmetallic materials. Many pure metals are too soft, corrode too easily or have other mechanical or chemical disadvantages that can be overcome if the metals are combined with other metals into alloys. Most alloys are harder than the metals from which they are made. They are also less malleable. They are harder to hammer into shape. Most alloys are less ductile than pure metals. That is, they are less easily drawn into fine wires and similar shapes. But most alloys are more fusible and more easily melted than the pure metals of which they are composed. Some alloys will even melt at the comparatively low temperature of hot water. Few alloys can conduct electricity as well as many metals in their pure forms. General effects of alloying elements are:

(i) Improves tensile strength without appreciably lowering ductility.
(ii) Improves toughness.
(iii) Improves hardenability which permits hardening of larger sections than possible with plain carbon steels or allows quenching with less drastic rates.
(iv) Reducing the hazard of distortion and quench cracking.
(v) Retain strength at elevated temperatures.
(vi) Obtain better corrosion resistance.
(vii) Improves wear resistance.

(viii) Imparts a fine grain structure to the steel.
(ix) Improves special properties such as abrasion resistance and fatigue behaviour.

In fact, the properties of alloys are quite dependent on the relationship between chemical compositions, processing and their microstructures. Alloyed steel in brief is made by adding a small percentage of alloying metals to liquid steel to subsequently alter the hardness, toughness, elasticity or durability. Naturally each of the alloying elements will have a specific property on the steel and are added to it in certain proportions on the different properties required. The different alloying elements used for enhancing various properties of steels are: (i) carbon, (ii) manganese, (iii) silicon, (iv) copper, (v) chromium, (vi) molybdenum, (vii) vanadium, (viii) nickel, (ix) aluminium, (x) boron, (xi) titanium, (xii) zirconium, (xiii) lead, (xv) nitrogen, (xvi) tungsten, etc.

### 1.4.1 Carbon

Carbon is an element whose presence is imperative in all steels. Indeed, carbon is the principle hardening element of steel and without carbon no steel is possible to form. That is, this alloying element determines the level of hardness or strength that can be attained by quenching. Furthermore, carbon is essential for the formation of cementite (as well as other carbides) and of pearlite, spheroidite, bainite and iron carbon martensite, with martensite being the hardest of the microstructures. Carbon is also responsible for increase in tensile strength, hardness, resistance to wear and abrasion. However, when present in high quantities it affects the ductility, the toughness and the machinability of steel. The effects of carbon on the tensile strength and elongation are shown below in Fig.1.10.

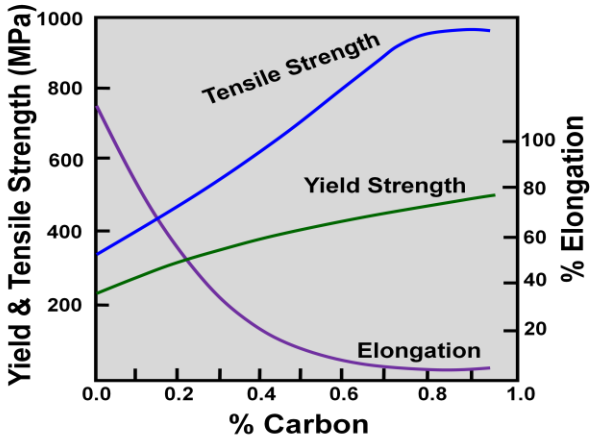



Figure 1.10: Effects of carbon on tensile strength and elongation of steels.

From Fig.1.10, it is clear that with increase in carbon both tensile and yield strength increase, however, ductility decreases. As the C content of the rimmed steels increases, surface quality deteriorates. Killed steels in the approximate range of 0.15–0.30%C may have poorer surface quality and require special processing to attain surface quality comparable to steels with higher

or lower C contents. Carbon has a moderate tendency for macro segregation during solidification and it is often more significant than that of any other alloying elements. Carbon has a strong tendency to segregate at the defects in steels (such as grain boundaries and dislocations). It is the main hardening element in all steels except the austenitic precipitation hardening (PH) stainless steels, marraging steels and interstitial free (IF) steels. The strengthening effect of C in steels consists of solid solution strengthening and carbide dispersion strengthening. Another important effect of higher C content in steel is its poor weldability.

### 1.4.2 Manganese

Manganese also contributes greatly towards increasing strength and hardness, but to a less extent than carbon. To be more precise, the degree to which manganese increases hardness and strength is dependent upon the carbon content of the steel. In fact, manganese contributes to the increasing the strength of the ferrite and also toward increasing the hardness of penetration of steel in the quench by decreasing the critical quenching speed. Moreover, steel consisting of a considerable amount of manganese can be quenched in oil rather than in water and are, therefore, less susceptible to cracking because of reduction in the shock of the quenching. This alloying is also considered as a degasifier reacting favourably with sulfur to improve forging ability and surface quality. This is achieved by interacting with the sulphur to give manganese sulphide. Naturally in doing so, the risk of hot shortness is considerably decreased. In addition, manganese enhances the tensile strength, the hardness, the hardenability and resistance to wear. A large amount (>2%) of Mn results in increased tendency toward cracking and distortion during quenching. The presence of Mn enhances the impurities such as P, Sn, Sb and As segregating to grain boundaries and induces temper embrittlement in steels. Manganese improves hot workability by preventing the formation of low-melting iron sulphide, FeS. Steels with a Mn/S ratio of at least 8/1 will not exhibit hot shortness. Mn/S, which forms preferentially to FeS, has a high melting point and appears in ingots as discrete and randomly distributed globules. Manganese has a negligible solid solution strengthening effect in austenite and only a moderate effect in ferrite. Tool and die steel steels should contain higher Mn for ensuring their deep hardening. This is important because, in most cases, these grade of steels contain high concentrations of strong carbide forming alloying elements, which can withdraw carbon from solid solution, thereby reducing hardenability.

### 1.4.3 Copper

Copper is added to steel to increase corrosion resistance. It also increases strength through precipitation hardening if present in concentrations greater than 0.75%. Copper produces these beneficial effects even though copper and iron have only very limited mutual solubility in both liquid and solid states. Maximum solubility of copper in austenite is 2.3% at 850$^{o}$C (1560$^{o}$F), rising to about 10% at 1450$^{o}$C (2650$^{o}$F). In ferrite, copper exhibits retrograde solubility to about 0.35% at low temperatures: this, plus the sluggish precipitation kinetics of primary (copper-rich) phase, makes age hardening copper steels possible. Copper does not interact with carbon as the

two elements are essentially immiscible. Therefore, all copper in mild steels will be dissolved or precipitated in ferrite, resulting in a slight hardening effect.

The presence of more than 0.2% Cu in steel produces a characteristic checking on forging surfaces. The degrees of this effect increases with copper and carbon content and with increasing preheat time and temperature, if heating is done in an oxidizing atmosphere. In this case, preferential oxidation of iron near the metal surface leaves a copper-enriched zone containing the low-melting phase on grain boundaries. In severe cases, the steel will be hot short and unworkable. Three solutions to this well-known problem are: (1) preheat only in protective or nonoxidizing atmospheres; (2) hot work only below 1090$^{o}$C (2000$^{o}$F), the melting point of the copper-rich phase; (3) add nickel or cobalt in amounts equal to about 1/3 to 1/2 the copper content as these metals raise the melting point of the copper phase. The third solution is most common and high copper steels will usually contain some nickel. As nickel content rises, so does the allowable forging/rolling temperature, although a practical limit in nickel content is signaled by the formation of a protective glaze at temperatures above 1280$^{o}$C (2150$^{o}$F). In this same context, it should be noted that copper steels should never be welded with an oxidizing oxyacetylene flame. This can also cause preferential oxidation of iron, copper enrichment and hot tearing. If oxidizing conditions are avoided, copper steels give excellent results will all welding processes.

### 1.4.4 Chromium

Chromium is one of the most versatile and widely used alloying elements in steel. It imparts corrosion and oxidation resistance, is a mild hardenability agent, improves wear resistance and promotes the retention of useful strength levels at elevated temperatures. When being present in reasonable quantities, chromium contributes much in reducing the quenching speed. In fact, such a slow quenching is achieved thereby enabling steel to be oil or air hardened. Chromium is an irreplaceable constituent in all stainless steels. Steels containing a minimum of about 12% chromium is considered stainless, i.e., resistant to oxidation and corrosion due to the existence of a thin but tightly adherent protective oxide layer on the steel's surface. In fact, over 70% of all chromium used in steelmaking is found in the many stainless grades. Next in tonnage consumption of chromium are the constructional alloy steels, most of which contain well less than 3% Cr. Tool steels, superalloys and other specialty metals, though often high in chromium content, are produced in smaller quantities and therefore rank lower in overall chromium application.

Chromium is medium carbide former. In the low Cr/C ratio range, only alloyed cementite $(Fe,Cr)_3C$ forms. If the Cr/C ratio rises, chromium carbides $(Cr,Fe)_7C_3$ or $(Cr,Fe)_{23}C_6$ or both, would appear. Chromium increases hardenability, corrosion and oxidation resistance of steels, improves high temperature strength and high pressure hydrogenation properties and enhances abrasion resistance in high carbon grades. Chromium carbides are hard and wear resistant and

increase the edge holding quality. Complex chromium iron carbides slowly go into solution in austenite; therefore, a longer time at temperature is necessary to allow solution to take place before quenching is accomplished. Chromium is the most important alloying element in steels. The addition of Cr in steels enhances the impurities, such as P, Sn, Sb, and As, segregating to grain boundaries and induces temper embrittlement.

### 1.4.5 Nickel

Nickel is a noncarbide forming element in steels. It is an austenite forming element, as a result addition of Ni open gamma phase field. Nickel raises hardenability. In any event, nickel is an austenite stabilizer, as is manganese, and in combination with Ni, Cr and Mo it tends to expand the gamma loop in the iron-carbon phase diagram (Fig.1.11). At very high concentrations (>30% Ni), no ferrite will be present at all. At lower nickel levels, the $A_3$ temperature will be depressed and in the presence of carbon, the $A_1$ temperature, as well. Nickel reduces the eutectoid carbon content, therefore, a nickel steel will contain proportionately more pearlite in its microstructure than a nickel-free steel of the same carbon content.

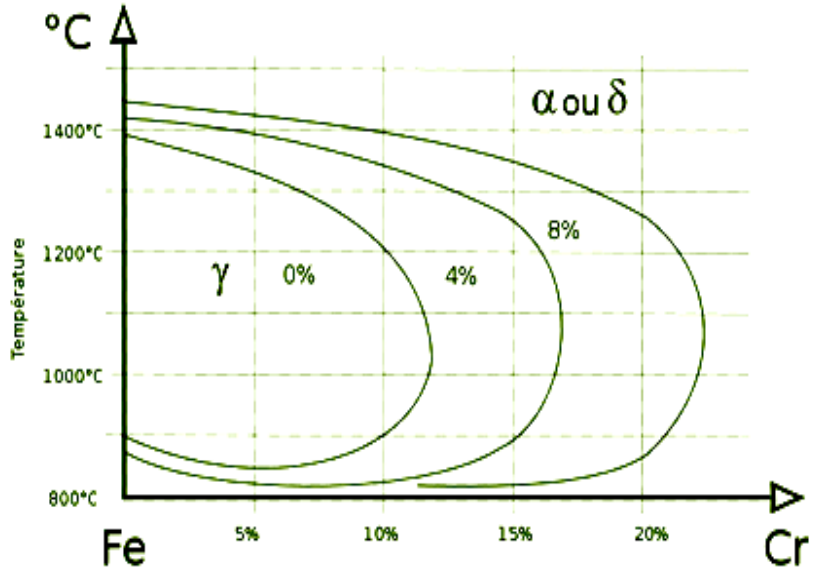



Figure 1.11: Interdependence between nickel and chromium on extent of gamma phase in steel.

Nickel is a weak hardenability agent and is rarely if ever used alone in conventional heat treatable alloy steels. However, it is often used in combination with other alloying elements such as chromium and vanadium or molybdenum to improve toughness. Nickel also does have profound effects on transformation characteristics when present in higher concentrations and these effects provide the basis for a number of interesting alloys. While its effects are not strong, nickel does have some influence on heat treating transformations. It retards both the pearlite and the bainite reactions. By the same token, nickel steels can often make do with a lower austenitizing temperature, the beneficial effects of which are a reduced tendency for distortion and/or cracking during quenching. Nickel addition increases strength without significant decrease in ductility, impact toughness and fatigue resistance of the steels. It decreases

FATT50%, even at the subzero temperatures. It also raises the corrosion resistance of the stainless steels.

### 1.4.6 Vanadium

Vanadium (V) is a very strong carbide former. Very small amounts of V dissolve in cementite. It dissolves in austenite, strongly increases hardenability, but the undissolved vanadium carbides decrease hardenability. Vanadium is a grain refiner and improves room temperature strength and hardness, Fig.1.12. Vanadium is also a strong nitride former. Fine vanadium carbides and nitrides give a strong dispersion hardening effect in microalloyed steels after controlled rolling and controlled cooling. Vanadium provides a very strong secondary hardening effect on tempering, therefore, it raises hot hardness and thus cutting ability in high speed steels. Vanadium increases fatigue strength and improves notch sensitivity. It increases wear resistance, edge holding quality and high temperature strength. It is, therefore, used mainly as an additional alloying element in high speed, hot forging and creep resistant steels. It promotes the weldability of heat treatable steels. The presence of V retards the rate of tempering embrittlement in Mo bearing steels. Vanadium also has another outstanding effect on steel that it helps controlling the grain growth during heat treatment. It is used rather in medium carbon steel where when added in relatively large quantities it causes a reduction in the hardenability of the steel because of excessive free vanadium in the matrix.

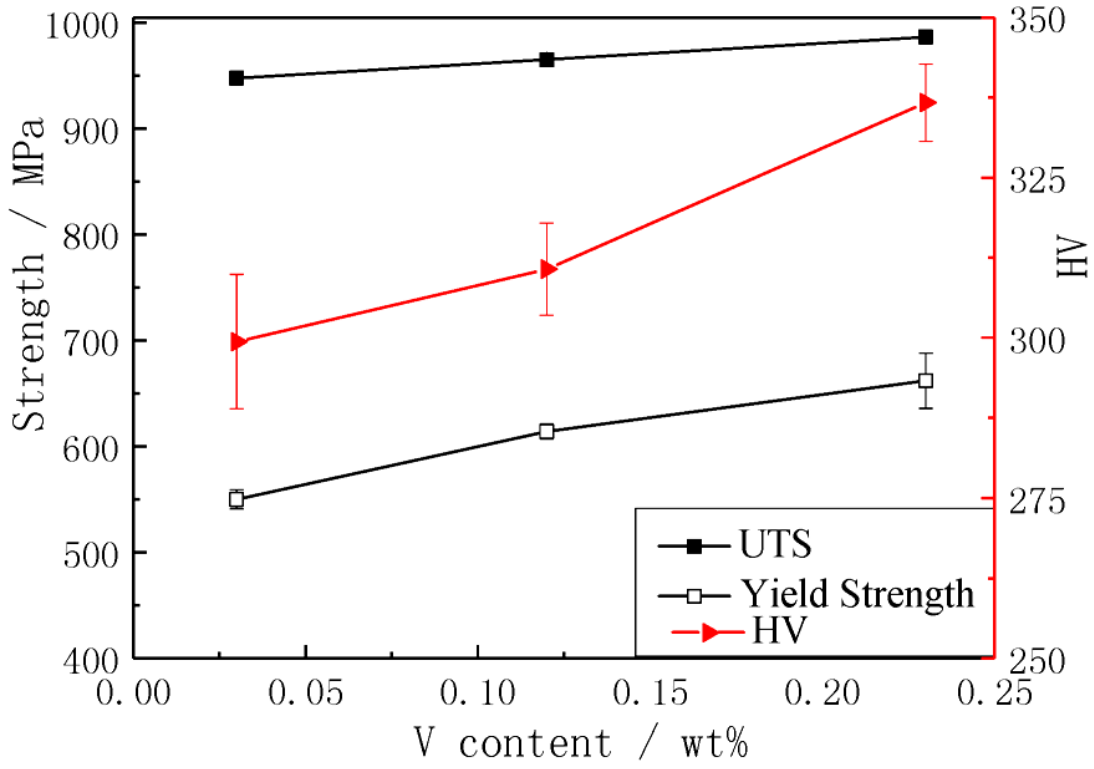



Figure 1.12: Effect of vanadium on strength and hardness of steels.

### 1.4.7 Molybdenum

Molybdenum (Mo) is a pronounced carbide former. It dissolves slightly in cementite, while molybdenum carbides will form when its content in steel is high enough. Molybdenum can induce secondary hardening during the tempering of quenched steels and improves the creep strength of low alloy steels at elevated temperatures. The addition of Mo produces fine grained steels, increases hardenability and improves fatigue strength. However, it delayed recrystallization that demand higher austenitizing temperature (Fig.1.13). Alloy steels containing 0.20–0.40% Mo display a delayed temper embrittlement, but cannot eliminate it. Molybdenum increases corrosion resistance and is used to a great extent in high alloy Cr ferritic stainless steels and with Cr–Ni austenitic stainless steels. High Mo contents reduce the susceptibility stainless steel to pitting. Molybdenum has a very strong solid solution strengthening in austenitic alloys at elevated temperatures. It is a very important alloying element for alloy steels.

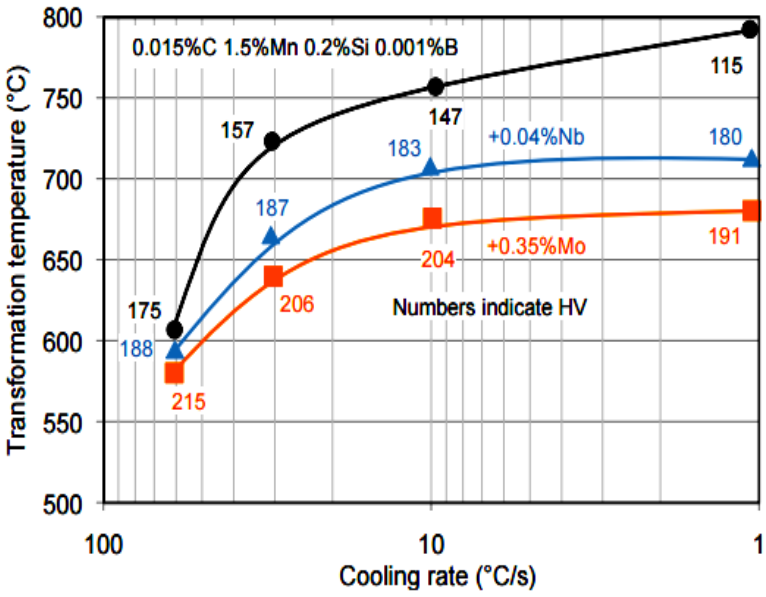



Figure 1.13: Effect of molybdenum on transformation temperatures of steels.

### 1.4.8 Tungsten

Tungsten (W) is known chiefly for its strong tendency to form extremely hard and stable carbides. This property, in fact, is the basis for the most important use of tungsten in steels: as a constituent of high speed and other tool steels. About 30% of all tungsten produced is used in this fashion. Carbide cutting tools account for one-half of the total tungsten market; alloy steels, superalloys, lamp filaments and miscellaneous applications make up the remainder.

Tungsten a strong carbide former. Tungsten slightly dissolves in cementite, it forms very hard, abrasion resistant carbides and can induce secondary hardening during the tempering of quenched steels. It promotes hot strength and red hardness and thus cutting ability. It prevents grain growth at high temperature.

### 1.4.9 Niobium and Tantalum

Niobium (Nb) and tantalum (Ta) are very strong carbide and nitride formers. Small amounts of Nb can form fine nitrides or carbonitrides and refine the grains (Fig.1.14).

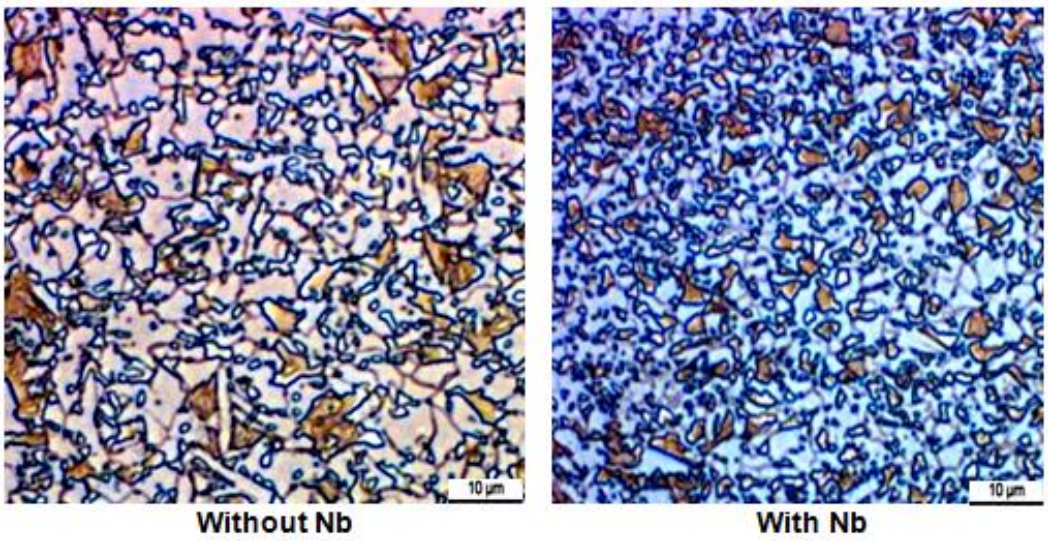



Figure 1.14: Microstructures of Nb free and Nb added steels.

Because of grain refinement effects, Nb increases yield strength, therefore, increases the ultimate tensile strength and toughness as well as fatigue property through controlled rolling and controlled cooling practices (Figs.1.15-16). A 0.03% Nb in austenite can increase the yield strength of medium carbon steel by 150 MPa. Niobium containing nonquenched and tempered steels, including microalloyed medium carbon steels and low carbon bainite (martensite) steels, offer a greatly improved combination of strength and toughness. Niobium is a stabilizer in Cr–Ni austenitic steels to eliminate intergranular corrosion. (0.065% Nb on C-Mn-Si microstructures).

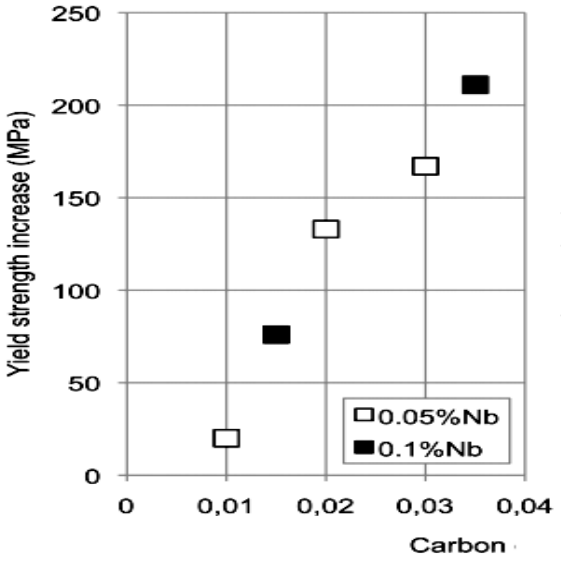



Figure 1.15: Effect of niobium on yield strength of plain carbon steels.

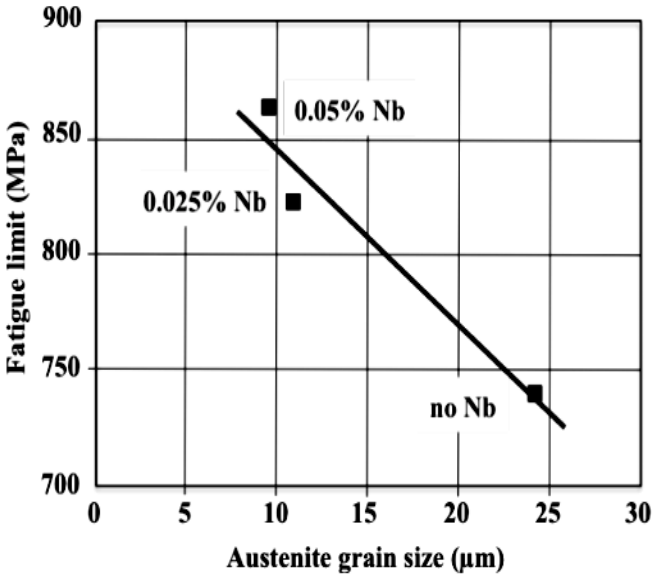



Figure 1.16: Effect of niobium on fatigue property of steel.

### 1.4.10 Titanium

Titanium (Ti) is a very strong carbide and nitride former. The effects of Ti are similar to those of Nb and V, but titanium carbides and nitrides are more stable than those of Nb and V. It is widely used in austenitic stainless steels as a carbide former for stabilization to eliminate intergranular corrosion. By the addition of Ti, intermetallic compounds are formed in maraging steels, causing age hardening. Titanium increases creep rupture strength through formation of special nitrides and tends significantly to segregation and banding. Ti, Nb and V are effective grain inhibitors because their nitrides and carbides are quite stable and difficult to dissolve in austenite. If Ti, Nb, and V dissolve in austenite, the hardenability of alloy steels may increase strongly due to the presence of Mn and Cr in steels. Mn and Cr decrease the stability of Ti, Nb and V carbides in steels.

### 1.4.11 Aluminium

Aluminium (Al) is widely used as a deoxidizer and a grain refiner. As Al forms very hard nitrides with nitrogen, it is usually an alloying element in nitriding steels. It increases scaling resistance and is, therefore, often added to heat resistant steels and alloys. In precipitation hardening stainless steels, Al can be used as an alloying element, causing precipitation hardening reaction. Aluminium is also used in maraging steels. Aluminum increases the corrosion resistance in low carbon corrosion resisting steels. Of all the alloying elements, Al is one of the most effective elements in controlling grain growth prior to quenching. Aluminum has the drawback of a tendency to promote graphitization.

### 1.4.12 Boron

Boron (Bo), is an alloying element that can be placed in the category of those whose main function is to enhance the hardenability of steel. However, the main interest in using boron to alloy steel is that it increases the hardenability of the material and this is, without having any effect on the ductility nor on the ferrite strength of the steel. As a result, formability and machineability of steel are boosted due to the presence of Boron. Indeed thus alloying element finds most of its applications in low carbon steels.

## 1.5 Classification of Steels

Steels can be classified by different systems depending on:

1. Compositions, such as carbon (or nonalloy), low alloy and high alloy steels.
2. Manufacturing methods, such as converter, electric furnace, or electroslag remelting methods.
3. Application or main characteristic, such as structural, tool, stainless steel or heat resistant steels.
4. Finishing methods, such as hot rolling, cold rolling, casting or controlled rolling and controlled cooling.
5. Product shape, such as bar, plate, strip, tubing or structural shape.
6. Oxidation practice employed, such as rimmed, killed, semikilled and capped steels.

7. Microstructure, such as ferritic, pearlitic, martensitic and austenitic.
8. According to standard specifications, as SAE, ASTM, AISI, DIN, JIS, BS, etc.
9. Heat treatment, such as annealing, quenching and tempering, air cooling (normalization) and thermomechanical processing.
10. Quality descriptors and classifications, such as forging quality and commercial quality.

Among the above classification systems, chemical composition is the most widely used basis for designation and is given due emphasis here.

Alloy steels may be defined as those steels that owe their improved properties due to the presence of one or more special elements or to the presence of large proportions of elements such as Mn and Si than are ordinarily present in carbon steels. Alloy steels contain Mn, Si or Cu in quantities greater than the maximum limits (e.g. 1.65% Mn, 0.60% Si and 0.60% Cu) of carbon steels or they contain special ranges or minimums of one or more alloying elements. Broadly, alloy steels can be divided into (1) low alloy steels containing less than 5 wt% total noncarbon alloy addition, (2) medium alloy steels containing 5–10 wt% total noncarbon alloy addition and (3) high alloy steels with more than 10 wt% total noncarbon alloy addition and microalloy with less than total 0.5% noncarbon alloying elements.

### 1.5.1 Low and Medium Alloy Steels

Low alloy steels constitute a group of steels that exhibit superior mechanical properties compared to plain carbon steels as the result of addition of such alloying elements as Ni, Cr and Mo. For many low alloy steels, the main function of the alloying elements is to increase the hardenability in order to optimize the strength and toughness after heat treatment. In some instances, however, alloying elements are used to reduce environmental degradation under certain specified conditions. Several special terms are used to de scribe various types of HSLA steels:

**a) Weathering Steels**: These group of steels contain ~0.1% C, 0.2–0.5% Cu, 0.5–1. 0% Mn, 0.05–0.15% P, 0.15–0.90% Si and sometimes contain Cr and Ni. They exhibit superior atmospheric corrosion resistance. Typical applications include railroad cars, bridges and unpainted buildings.
**b) Control Rolled Steels**: Steels designated to develop a highly deformed austenite structure by hot rolling (according to a predetermined rolling schedule) that will transform to a very fine equiaxed ferrite structure on cooling.
**c) Pearlite Reduced Steels**: Steels strengthened by very fine grained ferrite and precipitation hardening, but with low carbon content and therefore exhibiting little or no pearlite in the microstructure.
**d) Micro Alloyed Steels**: They are conventional HSLA steels containing V, Ti or Nb, as defined above. They exhibit discontinuous yielding behaviour.

**e) Dual Phase Steels**: Steels comprising essentially fine dispersion of hard strong martensite, but sometimes also retained austenite or even bainite in a soft and fine grained ferrite matrix. The volume function of martensite is about 20–30%. Steels are characterized by continuous yielding (i.e., no yield point elongation), low yield stress (the YS/UTS ratio being around 0.50), high UTS, superior formability and rapid initial work hardening rate. Additionally, they possess greater resistance to onset of necking (i.e., plastic instability) in the uniaxial sheet material forming process to provide large uniform strain.

### 1.5.2 Tool Steels

A tool steel is any steel used to shape other metals by cutting, forming, machining, battering or die casting or to shape and cut wood, paper, rock or concrete. Tool steels are usually designed to have high hardness and durability under severe service conditions. So, they comprise a wide range from plain carbon steels with up to 1.2% C without appreciable amounts of alloying elements to the highly alloyed steels in which alloying additions might reach to 50%. Although some carbon tool steel s an d low alloy tool steels have a wide range of carbon content, most of the higher alloy tool steels have a comparatively narrow carbon range. A mixed classification system is used to classify tool steels based on the use, composition, special mechanical properties or method of heat treatment.

High speed steels are used for applications requiring long life at relatively high operating temperatures such as for heavy cuts or high speed machining. High speed steels are the most important alloy tool steel s because of their very high hardness and goo d wear assistance in the heat treated condition and their ability to retain high hardness and the elevated temperatures often encountered during the operation of the tool at high cutting speeds. This red or hot hardness property is an important feature of high speed steels.

High speed steels are grouped into molybdenum type M and tungsten type T. Type M tool steels contain Mo,W, Cr, V, Mo and C as the major alloying elements, while type T tool steels contain W, Cr, V, Mo, Co, and C as the main alloying elements. In the United States, type M steels account for 95% of the high speed steels produced. There is also a subgroup consisting of intermediate high speed steels in the M group. The most popular grades among molybdenum types are M1, M2, M4, M7, M10 and M42, while those among tungsten types are T1 and T15. The main advantage of type M steels is their lower initial cost (approximately 40% cheaper than that of similar type T steels), but they are more susceptible to decarburizing, thereby necessitating better temperature control than type T steels. By using salt baths and sometimes surface coatings, decarburization can be controlled. The mechanical properties of type M and type T steels are similar except that type M steels have slightly greater toughness than type T steels at the same hardness level.

Hot work tool steels (AISI series) fall into three major groups: (1) chromium base, types H1–19, 2) tungsten base, types H20–H39 and (3) molybdenum base, types H40–H59. The distinction is based on the principal alloying additions; however, all classes have medium carbon content and Cr content varying from 1.75 to 12.75%. Among these steels, H11, H12, H13 are produced in large quantities. These steels possess good red hardness and retain high hardness (~50 Rc) after prolonged exposures at 500–550$^{o}$C. They are used extensively for hot work applications, which include parts for aluminium and magnesium die casting and extrusion, plastic injection molding, and compression and transfer mold.

Cold work tool steels comprise three categories: (1) air hardening, medium alloy tool steels (AISI A series), (2) high chromium tool steels (AISI D series) and (3) oil hardening tool steels (AISI O series). AISI A series tool steels have high hardenability and harden readily on air cooling. In the air hardened and tempered condition, they are suitable for applications where improved toughness and reasonably good abrasion resistance are required such as for forming, blanking and drawing dies. The most popular grade is A2. AISI D series tool steels possess excellent wear resistance and nondeforming properties, thereby making them very useful as cold work die steels. They find applications in blanking and cold forming dies, drawing and lamination dies, thread rolling dies, shear and slitter blades, forming rolls, and so forth. Among these steels, D2 is by far the most popular grade. AISI O series tool steels are used for blanking, coining, drawing, and forming dies and punches, shear blades, gauges and chuck jaws after oil quenching and tempering. Among these grades, O1 is the most widely used. Shock resisting tool steels (AISI S series) are used where repetitive impact stresses are encountered such as in hammers, chipping and cold chisels, rivet sets, punches, driver bits, stamps and shear blades in quenched and tempered conditions. In these steels, high toughness is the major concern and hardness the secondary concern. Among these grades, S5 and S7 are perhaps the most widely used.

Low alloy special purpose tool steels (AISI series) are similar in composition to the W type tool steels, except that the addition of Cr and other elements render greater hardenability and wear resistance properties, type L6 and the low carbon version of L2 are commonly used for a large number of machine parts. Mold steels (AISI P series) are mostly used in low temperature die casting dies and in molds for the injection or compression molding of plastics. Water hardening tool steels (AISI W series): Among the three compositions listed, W1 is the most widely used as cutting tools, punches, dies, files, reamers, taps, drills, razors, woodworking tools and surgical instruments in the quenched and tempered condition.

Alloying elements can be divided into two categories according to the interaction with carbon in steel:

1. Carbide forming elements, such as Mn, Cr, Mo, W, V, Nb, Ti and Zr. They go into solid solution in cementite at low concentrations. At higher concentrations, they form more stable alloy carbides, though Mn only dissolves in cementite.
2. Noncarbide forming elements, such as Ni, Co, Cu, Si, P and Al. They are free from carbide in steels and normally found in the matrix.

The table below shows summary of different effects of different alloying elements on the steel.

| Alloying element | Cr | Co | Mn | Mo | Ni | Ti | W | V |
|---|---|---|---|---|---|---|---|---|
| *Hardenability* | ++ | ... | ++ | ++ | + | ++ | ++ | +++ |
| *High temperature strength* | + | + | .... | ++ | ... | + | ++ | ++ |
| *Ductility and toughness* | ... | ... | + | ... | ++ | ... | ... | ... |
| *Abrasion resistance* | + | ... | ... | + | ... | + | ++ | + |
| *Fine austenite grain size* | ... | ... | ... | + | ... | ++ | + | +++ |
| *Corrosion resistance* | ++ | ... | ... | + | + | ... | ... | ... |

Steel is an alloy of iron and carbon. So, for better understanding of the heat treatment processes and various changes in microstructures associated with the heat treatment knowledge on the iron carbon diagrams, its various lines, phases, etc is very important. In the following section, a brief discussion on iron-carbon diagram and its associated subject matters.

### 1.6 The Iron–Carbon Phase Diagram

A portion of the iron–carbon phase diagram is presented in Fig.1.17.

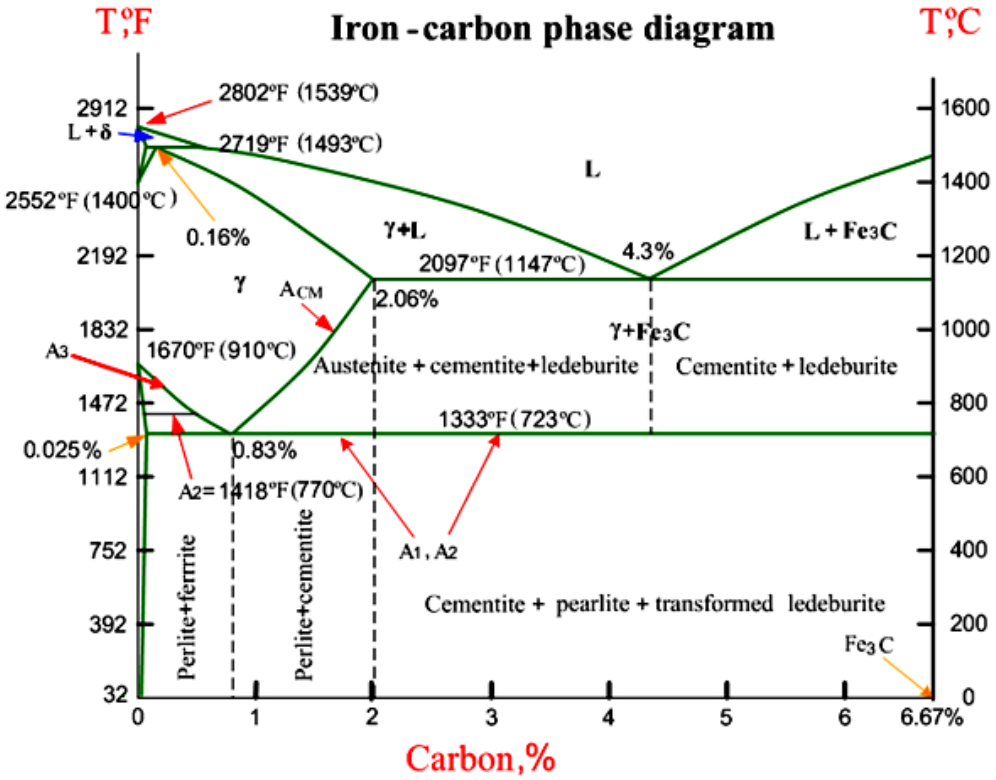



Figure 1.17: Iron-carbon phase diagram.

Pure iron, upon heating, experiences two changes in crystal structure before it melts. At room temperature the stable form, called ferrite or iron, has a BCC crystal structure. Ferrite experiences a transformation to FCC austenite or iron, at (910$^{o}$C). This austenite persists to 1400$^{o}$C, at which temperature the FCC austenite reverts back to a BCC phase known as δ (delta) ferrite, which finally melts at 1538$^{o}$C. All these changes are apparent along the left vertical axis of the phase diagram. Usually, the composition axis in Fig.1.17 extends only to 6.67 wt% C, because at this carbon concentration 100% iron carbon intermediate compound iron carbide or cementite ($Fe_3C$). In practice, all steels and cast irons have carbon contents less than 6.67 wt% C; therefore, we consider only the iron–iron carbide system.

Carbon is an interstitial type alloying element in iron and forms a solid solution with ferrites and austenite depending on the temperatures of the phases. In the BCC ferrite, only small concentrations of carbon are soluble; the maximum solubility is 0.025 wt% at 723$^{o}$C and at room temperature it is 0.008%. The limited solubility is explained by the shape and size of the BCC interstitial positions, which makes it difficult to accommodate the carbon atoms, Fig.1.18.

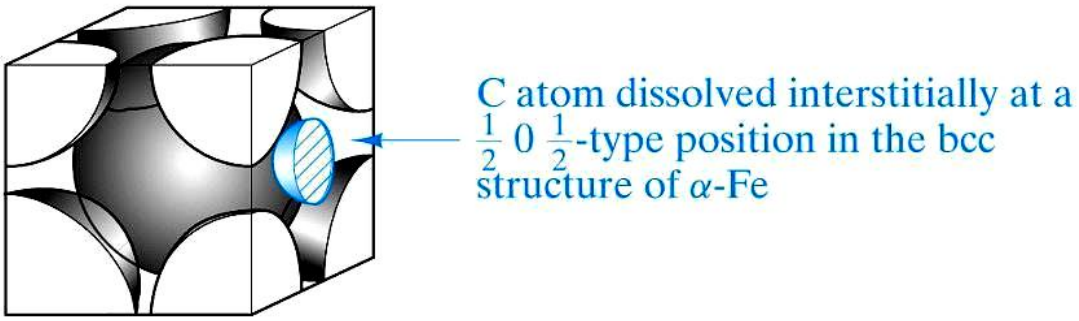



Figure 1.18: Possible interstitial position for carbon in BCC iron.

In the case of BCC type crystal, the packing factor is 0.68 that means there is 32% empty space at the interstitial position of iron cell. On the other hand, austenite has FCC crystal (Fig.1.19), where the packing factor is 0.74 that means there is only 26% empty space at the interstitial position. But carbon solubility in FCC iron is much higher than that of BCC iron. In BCC iron the total free space is distributed over six surfaces. The largest hole in the BCC ferrite is halfway between the centre of the face and the corner atoms. The possible vacant positions for the carbon atoms are on the front faces of the BCC ferrite. The largest interstitial atoms that could be fitted over there is 0.036nm. However, the atomic radius of carbon atom is 0.077nm, which is very difficult to be accommodated.

In the case of FCC iron, the atom inside the body is absent, Fig.1.19. The largest space in the FCC austenite is at the midway along the edge between corner atoms, which is bigger than that of the individual space in BCC iron. The largest interstitial sphere that would just fit is of radius 0.052nm. This large space is able to accommodate carbon atoms more easily (creating less strain at the surrounding areas) than that of ferrite. Moreover, with increase in temperature carbon

solubility in austenite increases up to 2.06% (~2.0%) at about 1140$^{o}$C because of difference in thermal expansion of iron and carbon (Note: that the thermal expansion co-efficients of pure iron and carbon, respectively, are $11.8x10^{-6}K^{-1}$ and $7.1x10^{-6}K^{-1}$). This solubility is approximately 100 times greater than the maximum for BCC ferrite. Even though present in relatively low concentration, carbon significantly influences the mechanical properties of ferrite.

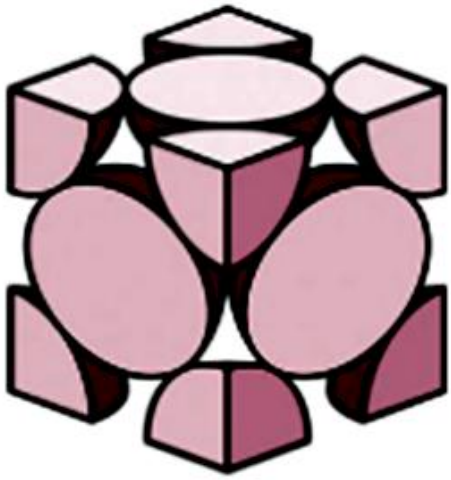


Figure 1.19: Interstitial positions in FCC iron.

The δ ferrite is virtually the same as ferrite, except for the range of temperatures over which each exists. Because of difference in thermal expansion of iron and carbon, the maximum solubility of carbon in δ ferrite is much higher (~0.1%) than that of ferrite (0.025%). Since the δ ferrite is stable only at relatively high temperatures, it is of no technological importance, because steels virtually have no use at this high temperature level. As a result, this has not discussed further.

Another solid phase in the iron-carbon phase diagram is cementite ($Fe_3C$). It forms when the solubility limit of carbon in ferrite exceeds. From iron-carbon phase diagram it is also clear that $Fe_3C$ will also coexist with the γ phase in between 727 and 1140$^{o}$C. Mechanically, cementite is very hard and brittle. The strength of some steels is greatly enhanced by its presence. Cementite is a metastable phase. At room temperature there is no problem related to its existence. It remains as a compound indefinitely at room temperature. However, if heated to between 650 and 700$^{o}$C for several years, it will gradually change or transform into iron and carbon, in the form of graphite, which will remain upon subsequent cooling to room temperature. In the iron-carbon diagram, three different isothermal reactions take place at three different carbon contents and temperatures which are:

1. Peritectic reaction
2. Eutectic reaction and
3. Eutectoid reaction

### 1.6.1 Peritectic Reaction

The reaction by that one liquid and one solid combine with each other to form a new solid on cooling or one liquid and one solid form a different type of solid on heating is called peritectic reaction. In the case of iron-carbon diagram this type of reaction takes place for 0.2% carbon content at about 1493$^{o}$C. Here, δ solid combines with liquid with subsequent formation of γ solid solution.

$$\delta\ Solid + Liquid\ (0.2\%C) \Leftrightarrow \gamma\ Solid$$

### 1.6.2 Eutectic Reaction

Here, from only one liquid two different solids are formed on cooling or from two different solids of different chemical compositions one liquid of average chemical compositions is formed. In the iron-carbon binary phase diagram, this reaction basically takes place for carbon content of cast iron range. At about 1140$^{o}$C, two different solids (cementite and ledeburite) are formed on cooling of only one liquid containing about 4.3%. The reaction is given below and the microstructures are presented in Fig.1.20.

$$One\ Liquid\ (4.3\%C) \Leftrightarrow Fe_3C + Ledeburite$$

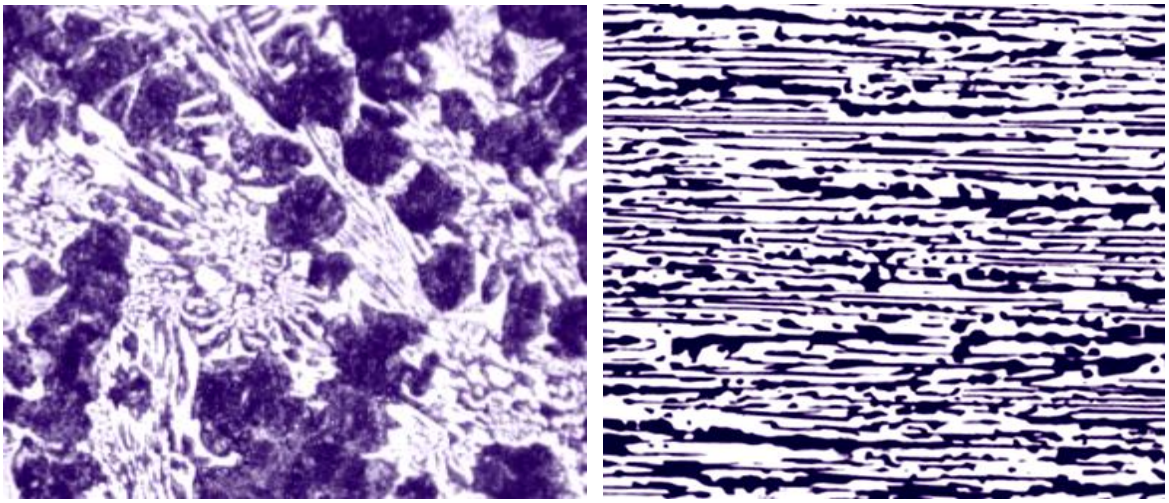


Figure 1.20: Eutectic microstructures consisting of lamellar cementite and austenite.

### 1.6.3 Eutectoid Reaction

In eutectoid reaction two different solids are formed from one another solid. This reaction is very important for steels. Almost all steels face this reaction when they are cooled from above the lower critical temperature (723$^{o}$C). In the iron-carbon diagram this reaction takes place for around 0.8% at 723$^{o}$C. In this reaction austenite having 0.8% carbon transforms to ferrite (0.025%C) and cementite (6.67%C) on cooling. Similarly, if one carbon steel consisting of having 0.8% carbon (whose microstructure is composed of ferrite and cementite) is heated then an isothermal reaction will take place at 723$^{o}$C with subsequent formation of austenite having

exactly 0.8% carbon. The reaction is shown below and developed microstructure is presented in Fig.1.21.

$$One\ Solid\ (austenite\ with\ 0.8\%C) \Leftrightarrow Ferrite\ (0.025\%C) + Fe_3C\ (6.67\%C)$$

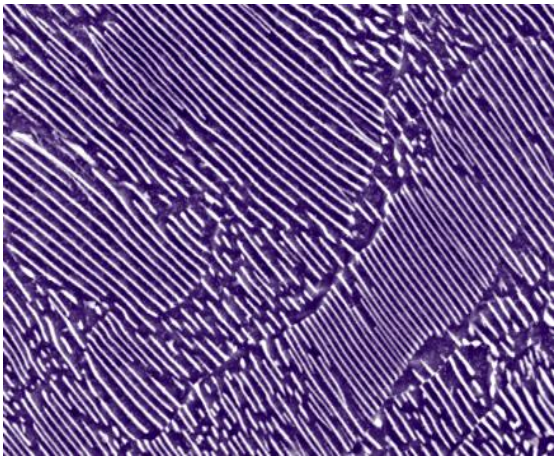


Figure 1.21: Eutectoid microstructures consisting of lamellar cementite and pearlite.

The eutectoid phase changes described in the above equation are very important, being fundamental to the heat treatment of steels. This will be explained and discussed in the subsequent chapter.

### 1.7 Influence of Other Alloying Elements on Fe-C Phase Diagram

The extent of these alterations of the positions of phase boundaries and the shapes of the phase fields depends on the particular alloying element and its concentration. One of the important changes is the shift in position of the eutectoid with respect to temperature and to carbon concentration. Almost all alloying elements reduce the requirement of carbon content for eutectoid compositions. In this respect, Ti, W and Mo have a very strong effect, Fig.1.22.

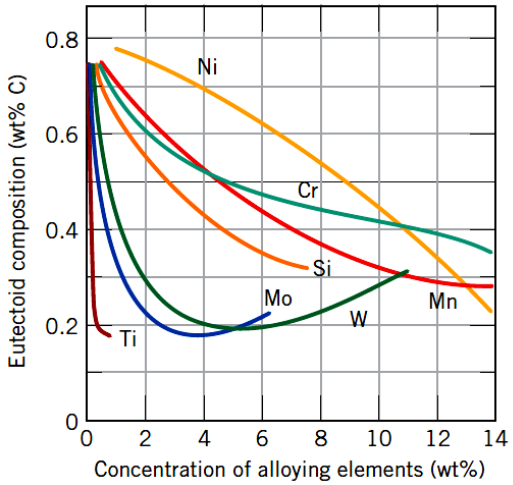



Figure 1.22: Effect of alloying elements on eutectoid carbon content.

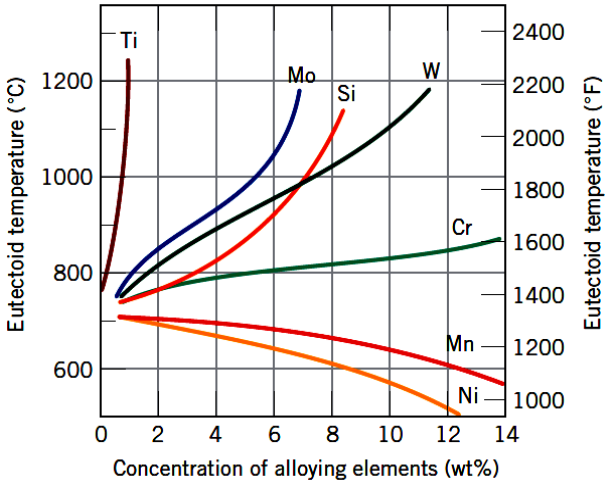



Figure 1.23: Effect of alloying elements on eutectoid transformation temperature.

Another important change in the phase diagram is the shift of eutectoid temperature, Fig.1.23. Some elements tend to increase the eutectoid temperature. In this point of view, Ti, Mo, W and Si are very strong. These alloying elements usually provide high temperature service properties of steel components. There are also some alloying elements (Ni, Mn) that reduce the eutectoid temperature. Alloying elements in this group are limited. With the additions of these alloying elements, it has been possible to make the austenite phase stable at room temperature and also to develop fully austenitic grade of (austenitic stainless steel, superalloy, etc). Thus, other alloy additions alter not only the temperature of the eutectoid reaction but also the relative fractions of pearlite and the proeutectoid phase that form.

## 1.8. Development of Microstructure in Iron–Carbon Alloys

### 1.8.1 Eutectoid Steel

For iron-carbon alloy, the final microstructures depend on both the carbon content and heat treatment. In this chapter development of microstructures through very slow cooling of steel alloys, in which equilibrium is continuously maintained will be discussed. A more detailed exploration of the influence of heat treatment on microstructure and ultimately on the mechanical properties of steels has been discussed in heat treatment chapter.

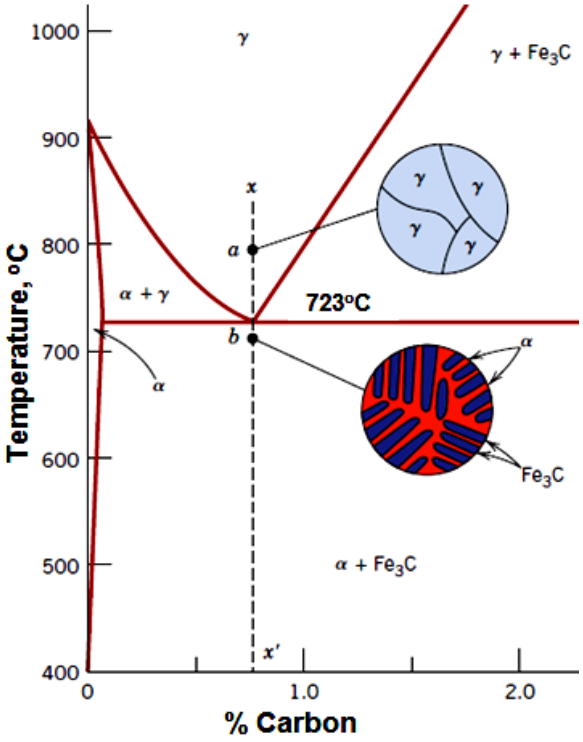



Figure 1.24: Slow cooling and development of microstructures in eutectoid steel.

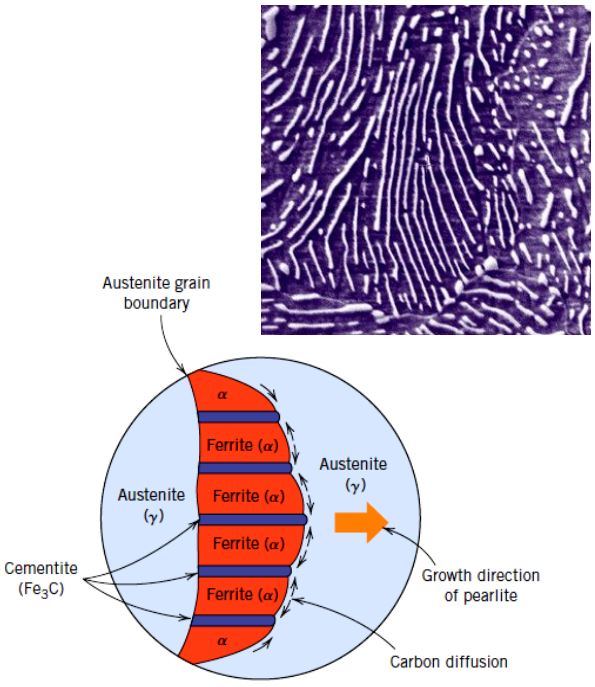



Figure 1.25: Growth of ferrite and cementite during slow cooling of eutectoid steel and layered cementite in final microstructures.

At first consider the slow cooling of iron carbon alloy having eutectoid composition (eutectoid steel contains around 0.8%C). It has been mentioned that steel is an alloy of iron and carbon having maximum carbon content 2.0% (see Fe-C diagram). Suppose that this alloy is cooled

from 800°C, where the phase is completely austenitic. As the alloy is cooled, there will be no change in the phase until the eutectoid temperature (723°C) is reached. Upon crossing this temperature to point b, the austenite transforms according to equation presented for eutectoid reaction in the earlier section, Fig.1.24. The microstructure for this eutectoid steel that is slowly cooled through the eutectoid temperature consists of alternating layers of the two phases (ferrite and $Fe_3C$, which is called pearlite) that form simultaneously during the transformation. In this case, the thickness of ferrite layer will be significantly higher (Fig.1.25) than that of cementite because small amount cementite formation cause major imbalance in the carbon content of the alloy.

Figure 1.21 is a real microstructure of slowly cooled eutectoid steel. The pearlite exists as grains in various orientations. The thick light layers are the ferrite phase and the cementite phase appears as thin lamellae most of which appear dark. Mechanically, pearlite has properties intermediate between the soft, ductile ferrite and the hard, brittle cementite. The tensile strength of ferrite and cementite are, respectively, 40,000 and 5000 psi. However, the tensile strength of pearlite is 120,000 psi. In this sense, pearlite is a metal matrix composite, where soft ferrite behaves as a matrix and cementite behaves as a reinforcing material.

### 1.8.2 Hypoeutectoid Steel

Eutectoid steels are those iron-carbon alloys where carbon contents are less than eutectoid carbon, i.e. less than o.8%C. Development of microstructures in this type of steel will now be discussed. Consider a composition to the left of the eutectoid, between 0.025 and 0.76 wt% C; e.g. 0.25%. Cooling an alloy of this composition is represented by moving down the vertical line in Fig.1.26. When the temperature is just below the OM line, then α phase will start to form at grain boundaries. This α phase contains much lower carbon than the average carbon content. So, rest of the austenite will have more carbon. With decrease in temperature, ferrites at austenite grain boundaries will grow causing more carbon content in the rest of austenite. This gradual increase in fraction of ferrite area and increase in carbon content in the rest of austenite will continue until eutectoid temperature (723°C) is reached when carbon content in the austenite will reach to eutectoid carbon content (0.8%). At this point eutectoid reaction will take place with the formation of layered ferrite and cementite, which is termed as pearlite. So, just below the lower critical line (eutectoid temperature line), e.g. at point f the microstructures of this hypoeutectoid steel will be composed of proeutectoid ferrite and pearlite. Pearlite also has ferrite platelets, which are called eutectoid ferrite. Similarly, cementite platelets in the pearlite are termed as eutectoid cementite.

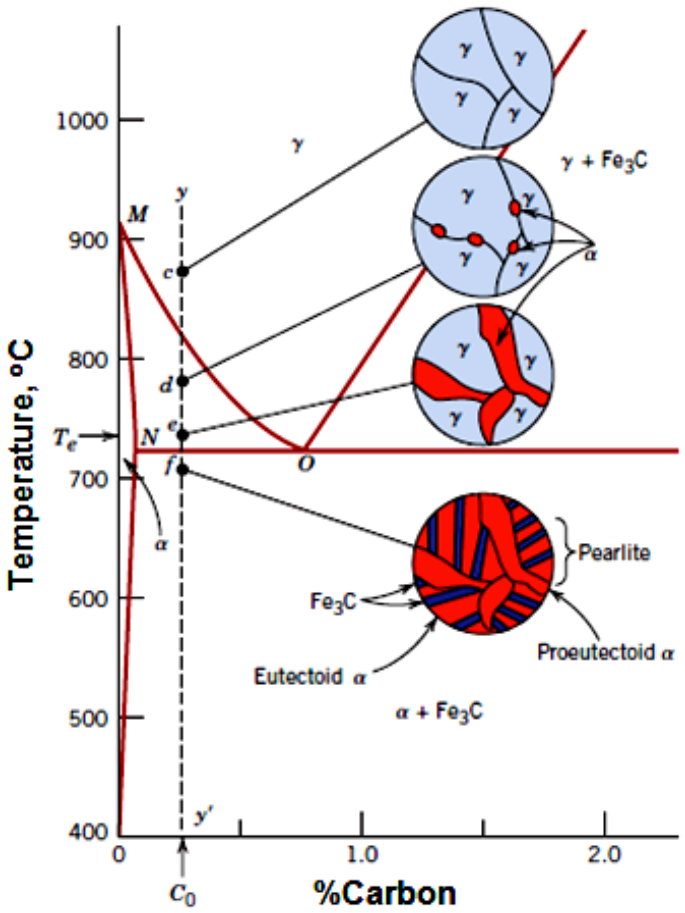



Figure 1.26: Development of microstructures in hypoeutectoid steel.

After point f, on cooling, there will be no further change in the microstructures. Real microstructures of a typical hypoeutectoid steel is shown in Fig.1.27.

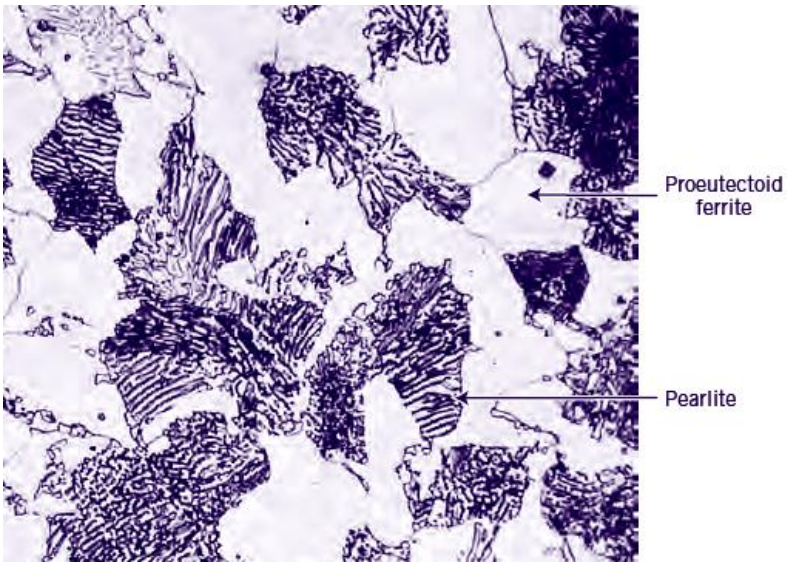



Figure 1.27: Typical microstructures in hypoeutectoid steel.

### 1.8.3 Hypereutectoid Steel

The slow cooling of a hypereutectoid steel is shown in Fig.1.28.

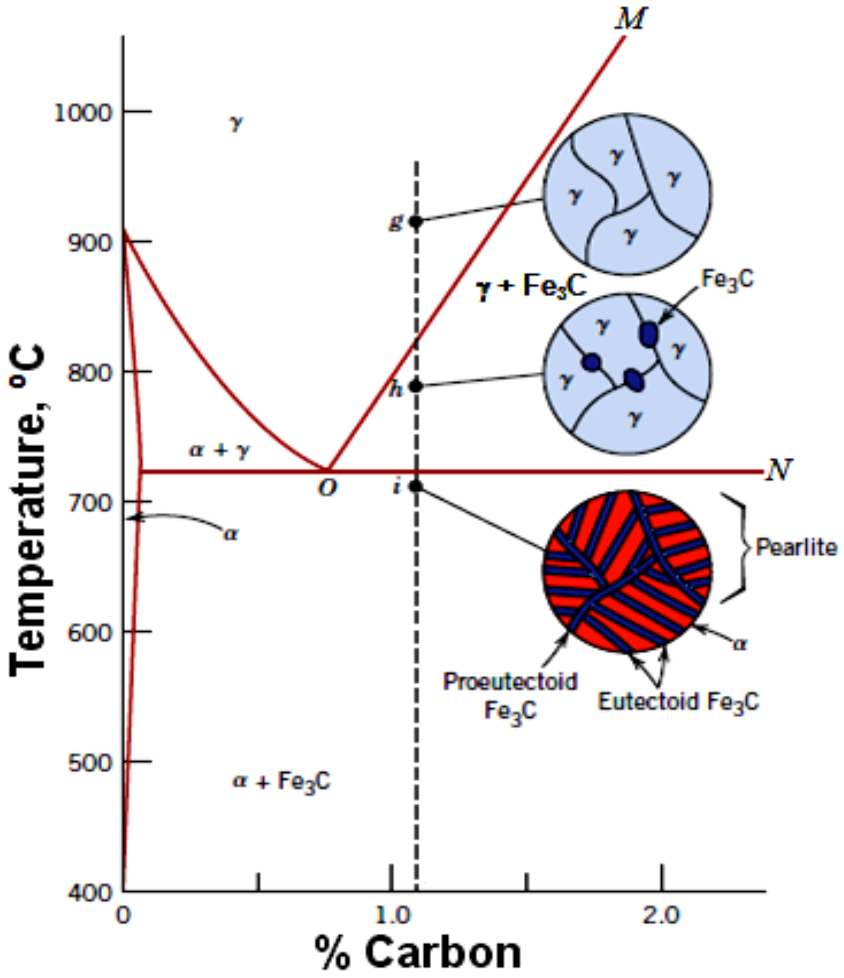



Figure 1.28: Development of microstructures in hypereutectoid steel.

Hypereutectoid steels are those steels, where the carbon contents are more than 0.8%. This means, during cooling, one proeutectoid phase must be precipitated at grain boundaries of initial austenite that will gradually reduce carbon content in the rest austenite. This gradual decrease in carbon content will finally result eutectoid carbon content in the austenite to start eutectoid reaction at lower critical temperature (at around 723$^{o}$C). Let us consider a hyper eutectoid steel containing 1.10% carbon, which is cooled from its single γ phase (point g in Fig.1.28) to room temperature.

From Fig.1.28, it is clear that if the steel is cooled from g to below the upper critical line (line OM), e.g. to temperature at point h, then precipitation of cementite grain will take place at grain boundaries of prior austenite. The carbon content of cementite ($Fe_3C$) is 6.67, which means that formation of small amount of cementite will significantly decrease in the carbon content of the rest of austenite. Further cooling will increase the proportion of proeutectoid cementite and

decrease in austenite content. With decrease in temperature this type of transformation continues until the eutectoid carbon content (0.8%C) is achieved in the rest austenite. At eutectoid carbon content, which is achieved at just over the lower critical temperature line (*ON*), pearlite will form from the rest of austenite following the rule of eutectoid reaction. So, just below the lower critical temperature (e.g. at point i) line, the microstructures of slowly cooled hyper eutectoid steel will be composed of proeutectoid cementite (which is proeutectoid ferrite in the case of hypoeutectoid steel) and pearlite, Fig.1.28. Further cooling from point I, no change in the microstructures will take place as both phases (cementite and pearlite) are stable at room temperature. Finally, the microstructures of slowly cooled hypereutectoid steel will be composed of proeutectoid cementite network around pearlite grains as shown in Fig.1.29.

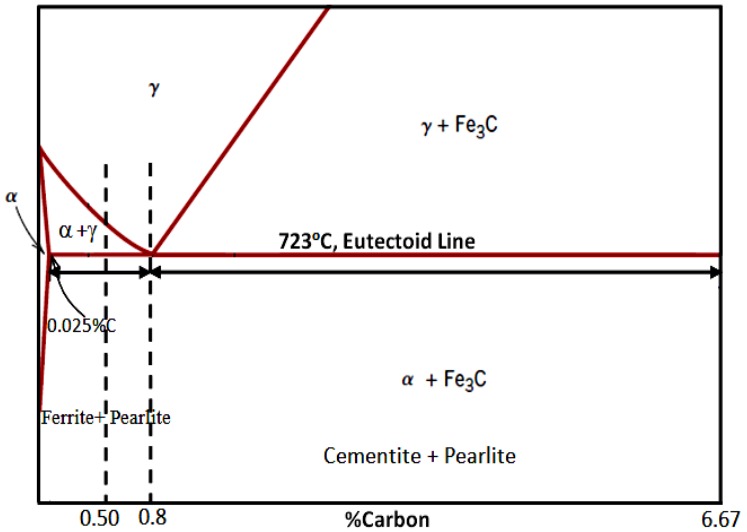
Figure 1.29: Microstructures of a slowly cooled hypereutectoid steel.

**Problem 1.1:** For a 99.50 wt% Fe–0.50 wt% C alloy at a temperature just below the eutectoid as shown in the following figure, determine the following:

(a) The fractions of total ferrite and cementite phases

(b) The fractions of the proeutectoid ferrite and pearlite

(c) The fraction of eutectoid ferrite



(a) As per lever rule for 0.5%C

$$W_{\alpha(total)} = \frac{6.67 - 0.50}{6.67 - 0.025} = 0.93$$

$$and \quad W_{Fe3C} = \frac{0.50 - 0.025}{6.67 - 0.025} = 0.07$$

(b) For fractions of proeutectoid ferrite and pearlite for just less than 0.8%C:

$$W_P = \frac{0.50 - 0.025}{0.80 - 0.025} = 0.61 \qquad and \qquad W_{\alpha(pro)} = \frac{0.80 - 0.50}{0.80 - 0.025} = 0.39$$

(c) Ferrite might remain in free form (proeutectoid ferrite) as grains and combined form in pearlite (eutectoid ferrite) as platelets. So, total ferrite will be:

$$W_{\alpha(pro)} + W_{\alpha(eu)} = W_{\alpha(total)}$$

$$or \quad W_{\alpha(eu)} = W_{\alpha(total)} - W_{\alpha(pro)} = 0.93 - 0.39 = 0.54$$

### 1.9 Types of Heat Treatment

There are several types of heat treatment, however, the most common heat treatments used for the modification of steel properties are:

| | |
|---|---|
| A. Annealing | B. Normalizing, |
| C. Hardening | D. Tempering |
| E. Martempering | F. Austempering |

#### 1.9.1 Annealing

Annealing is a heat treatment process where a material is exposed to a moderate to elevated temperature for an extended time period and then slowly cooled, generally in the furnace. Ordinarily, annealing is carried out to (1) relieve stresses; (2) increase softness, ductility and toughness, and/or (3) produce a specific microstructure. A variety of annealing heat treatments are possible. Any annealing process consists of three stages: (1) heating to the desired temperature, (2) holding or “soaking” at that temperature and (3) slow cooling, usually to room temperature. Time is an important parameter in these procedures. During heating and cooling, there exists temperature gradients between the outside and interior portions of the piece; their magnitudes depend on the size and geometry of the piece. If the rate of temperature change is too great, temperature gradients and internal stresses may be induced that may lead to warping or even cracking. Also, the actual annealing time must be long enough to allow for any necessary

transformation reactions. Depending on the targeted purposes of heat treatment, annealing might be of the following four categories:

A. Full annealing
B. Process annealing
C. Stress relief annealing
D. Spheroidizing

### 1.9.1.1 Full Annealing

It is a heat treatment technique used usually for hypoeutectoid steels (low and medium carbon steels) that will be machined or will experience extensive plastic deformation during a forming operation or for as cast products where the mechanical property is inferior because of coarse grained structure with inhomogeneous chemical compositions, Fig.1.30.

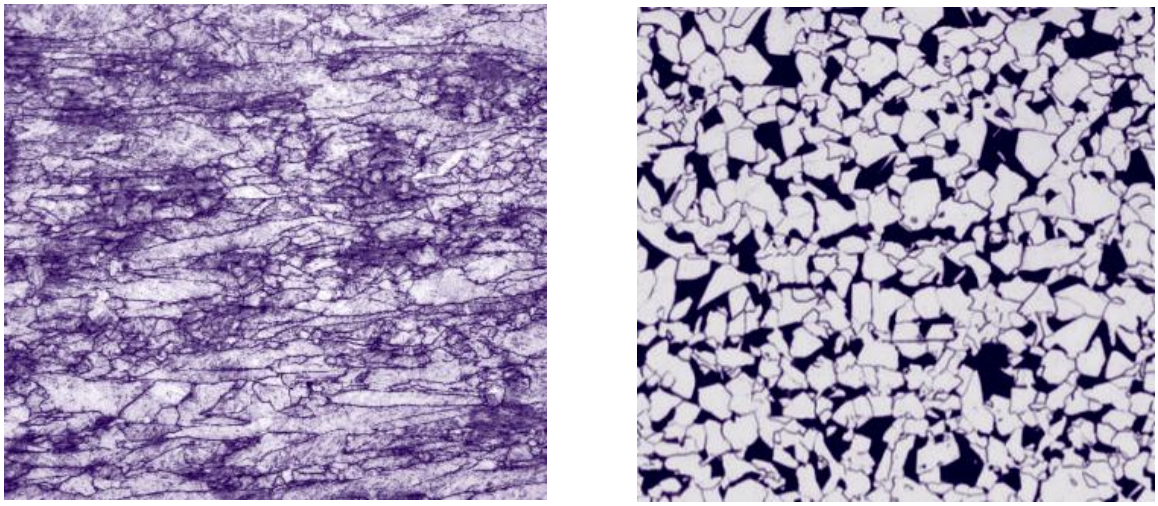


Figure 1.30: Microstructures of as cast (inhomogeneous, left) mild steel and after annealing (right).

This heat treatment is also used to relieve internal stresses induced by rolling, forging or to remove coarseness of grains in the as cast products. In general, the alloy is treated by heating to a temperature of about 30-40$^{o}$C above the $A_3$ line to form full austenite. In the case of hypereutectoid steel, this heat treatment is not usually practiced, where spheroidizing annealing is preferred. However, if necessary, a temperature 30-50$^{o}$C above the $A_1$ line is selected (to form austenite and $Fe_3C$ phases), Fig.1.31. It is held at this temperature for sufficient time for all the material to transform into austenite or austenite-cementite as the case may be. The second step is holding the steel component at this temperature for a definite holding (soaking) period of at least 20 minutes per cm of the thick section to assure equalization of temperature throughout the cross section of the component and complete austenite formation.

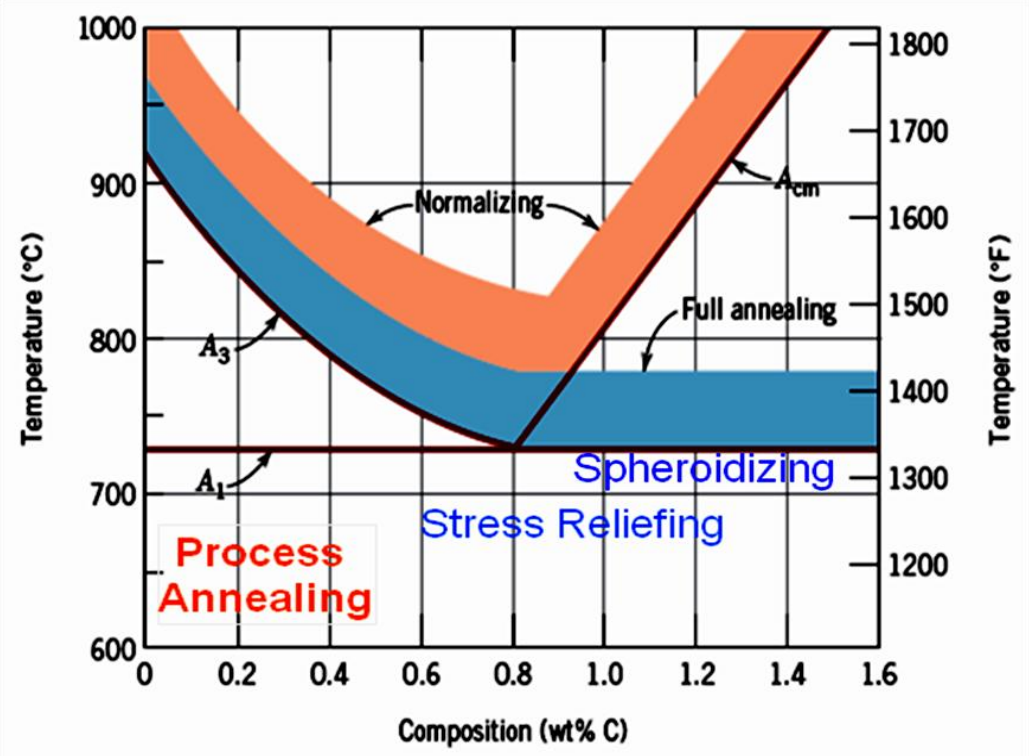



Figure 1.31: Temperature selection for various steels for different annealing processes.

It is then slowly cooled at a rate of about 20ºC/hr in a furnace to about 500ºC into the ferrite-cementite range. At this point, it can be cooled in room temperature air with natural convection. The grain structure might be coarse pearlite with ferrite or cementite (depending on whether hypo or hyper eutectoid). The steel becomes soft and ductile. It is possible to calculate upper and lower critical temperatures using the actual chemical composition of the steel. The following equations will give an approximate critical temperature for hypoeutectoid steel:

$$A_1(°C) = 723 - 20.7(\%Mn) - 16.9(\%Ni) + 29.1(\%Si) + 16.9(\%Cr)$$

$$A_3(°C) = 910 - 203\%C - 15.2(\%Ni) + 44.7(\%Si) + 104(\%V) + 31.5(\%Mo)$$

Some mechanical properties of pearlite formed during slow cooling of eutectoid (0.80% of carbon) steel are approximately as follows:

Tensile strength: 110,000 lb/in$^2$
Yield strength: 70,000 lb/in$^2$
Brinel hardness number: 200

**Problem 1.2**: Calculate the full annealing temperatures for steels of the following AISI-SAE Numbers.

**TABLE 12-1 ■ *Compositions of selected AISI-SAE steels***

| AISI-SAE Number | % C | % Mn | % Si | % Ni | % Cr | Others |
|---|---|---|---|---|---|---|
| 1020 | 0.18–0.23 | 0.30–0.60 | | | | |
| 1040 | 0.37–0.44 | 0.60–0.90 | | | | |
| 1060 | 0.55–0.65 | 0.60–0.90 | | | | |
| 1080 | 0.75–0.88 | 0.60–0.90 | | | | |
| 1095 | 0.90–1.03 | 0.30–0.50 | | | | |
| 1140 | 0.37–0.44 | 0.70–1.00 | | | | 0.08–0.13% S |
| 4140 | 0.38–0.43 | 0.75–1.00 | 0.15–0.30 | | 0.80–1.10 | 0.15–0.25% Mo |
| 4340 | 0.38–0.43 | 0.60–0.80 | 0.15–0.30 | 1.65–2.00 | 0.70–0.90 | 0.20–0.300% Mo |
| 4620 | 0.17–0.22 | 0.45–0.65 | 0.15–0.30 | 1.65–2.00 | | 0.20–0.30% Mo |
| 52100 | 0.98–1.10 | 0.25–0.45 | 0.15–0.30 | | 1.30–1.60 | |
| 8620 | 0.18–0.23 | 0.70–0.90 | 0.15–0.30 | 0.40–0.70 | 0.40–0.60 | 0.15–0.25% Y |
| 9260 | 0.56–0.64 | 0.75–1.00 | 1.80–2.20 | | | |

The amount of pearlite present in a slowly cooled hypoeutectoid steel is a linear function of the carbon content, varying from no pearlite, when no carbon is present (the very slight amount of carbon soluble in alpha iron may be neglected), to all pearlite at 0.80 percent of carbon, Fig.1.32. The balance of the structure of hypoeutectoid steels is composed of ferrite. Since the mechanical properties of aggregates of ferrite and pearlite are functions of the relative amounts of these two constituents, the mechanical properties of slowly cooled hypoeutectoid steels are also linear functions of the carbon content, varying between those of iron at no carbon to those of pearlite at 0.80 percent of carbon (Fig.1.33).

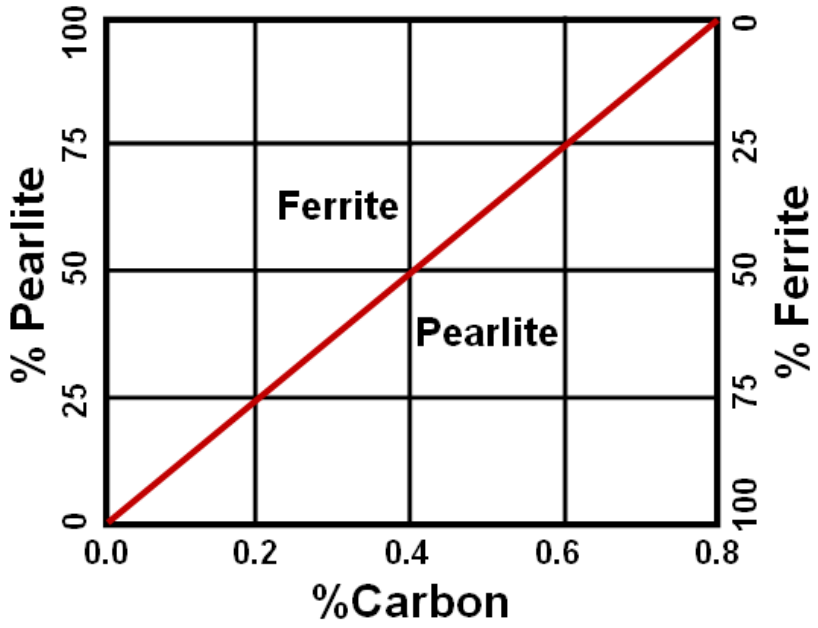



Figure 1.32: Effect of carbon content on proportion of ferrite and pearlite.

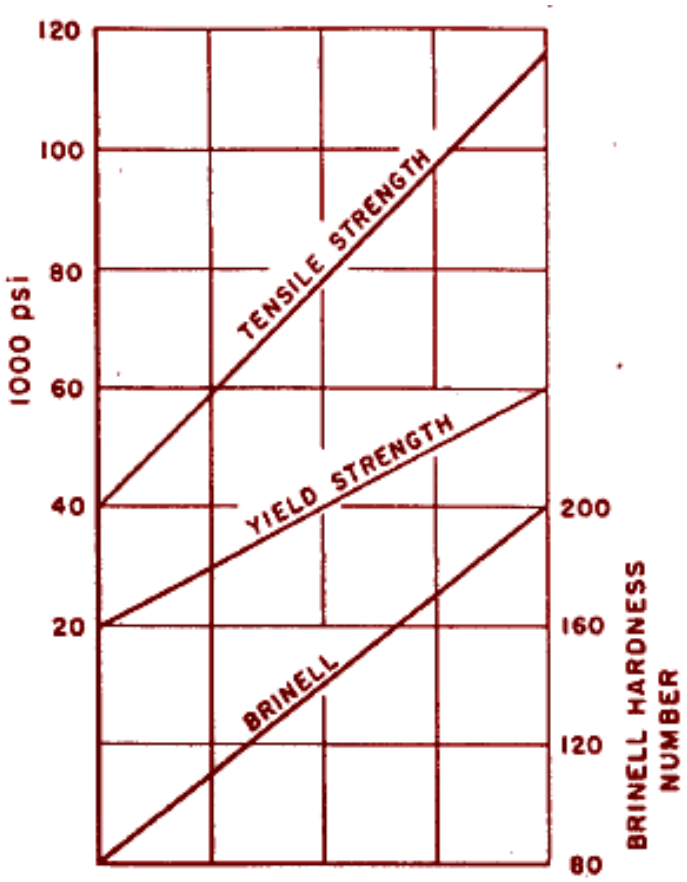



Figure 1.33: Effect of carbon content on tensile strength and hardness of steel

For full annealed steel containing up to 0.8% carbon, qualitative tensile strength is possible to calculate from the following relationship:

**Ultimate tensile strength (in psi) = Fraction of Ferrite x 40,000 + Fraction of Pearlite x 120,000**

Here it is to be mentioned that the tensile strength of the hypereutectoid steel is not possible to know from the above relationship because cementite has a very low tensile strength and that its effect on strength is much morphology controlled not the amount of the cementite.

**Problem 1.3:** For a 99.50 wt% Fe–0.50 wt% C alloy at a temperature just below the eutectoid as shown in the following figure, determine the tensile strength of the steel in full annealed condition.

**Solution**: The fractions of proeutectoid ferrite and pearlite are determined similarly by employing lever rule. As proeutectoid ferrite forms only for carbon content just less than 0.8%C, so, in this case, the tie line should extend only to the eutectoid composition. So, as per lever rule:

$$W_P = \frac{0.50 - 0.025}{0.80 - 0.025} = 0.61$$

$$and \qquad W_{\alpha(pro)} = \frac{0.80 - 0.50}{0.80 - 0.025} = 0.39$$

**Now, the ultimate tensile strength (in psi) = Fraction of Ferrite x 40,000 + Fraction of Pearlite x 120,000**

**= 0.39x40000 + 0.61x120000**
**= 15,600 + 73,200**
**= 88,800 psi or 612 MPa**

**Now, the approximate yield strength (YS) of the steel = 0.5xUTS = 306 MPa**

### 1.9.1.2 Process Annealing

Process annealing is a heat treatment technique that is used to negate the effects of cold work, that is, to soften and increase the ductility of a previously strain hardened metal for further cold working, Fig.1.34.

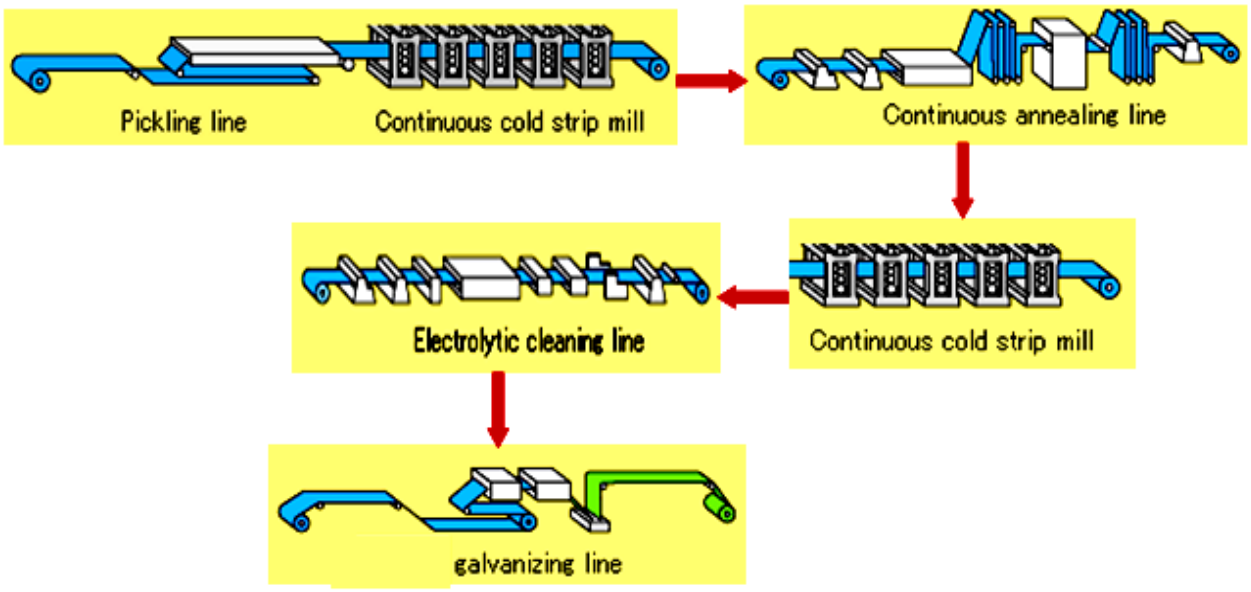



Figure 1.34: Flow diagram showing the process annealing used for production of thin sheet.

It is commonly utilized during fabrication procedures that require extensive plastic deformation to allow a continuation of deformation without fracture or excessive energy consumption in the production process. Because, after extensive cold working, the materials lose almost all of its ductility level, Fig.1.35. As this type of annealing is practiced during industrial process, so it is named as process annealing. Process annealing is a very useful heat treatment for production of thin wire and sheet products.

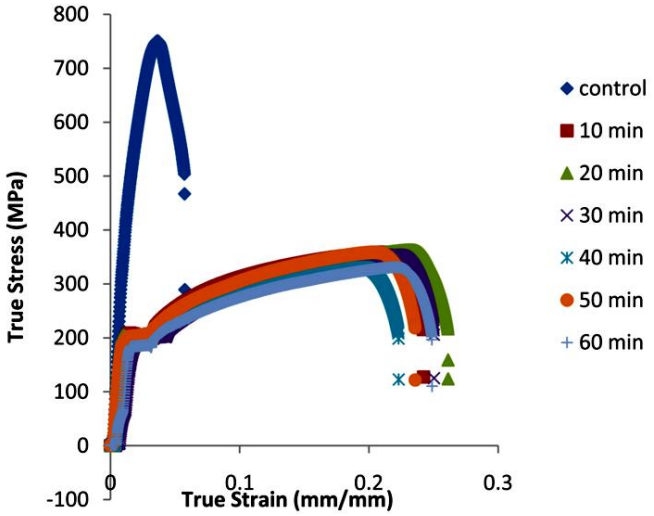



Figure 1.35: Effect of degree of cold working on the tensile behaviours of a typical carbon steel.

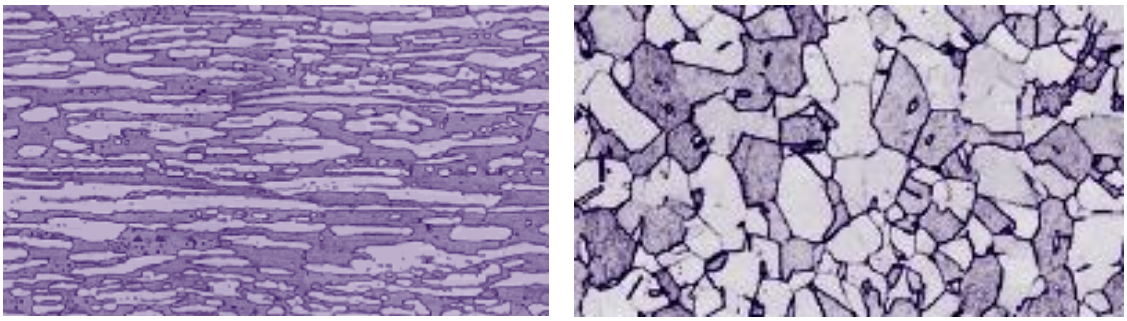


Figure 1.36: Effect of process annealing on the microstructures of a mild steel sheet.

Ordinarily a fine grained microstructure is desired, therefore, the heat treatment is terminated before appreciable grain growth. Since the material stays in the same phase throughout the process, the only change that occurs is the size, shape and distribution of the grain structure, Fig.1.36. This process is cheaper than either full annealing or normalizing since the material is not heated to a very high temperature or cooled in a furnace. It has been mentioned that this annealing heat treatment is usually performed during thin wire and sheet production, where surface oxidation at high temperature might deteriorate the properties of the product. As a result, process annealing is usually carried out at relatively lower temperature. If high temperature is essential during any process annealing nonoxidizing atmosphere should be ensured. The overall effects of cold working and subsequent process annealing on microstructures and properties are shown in Fig.1.37.

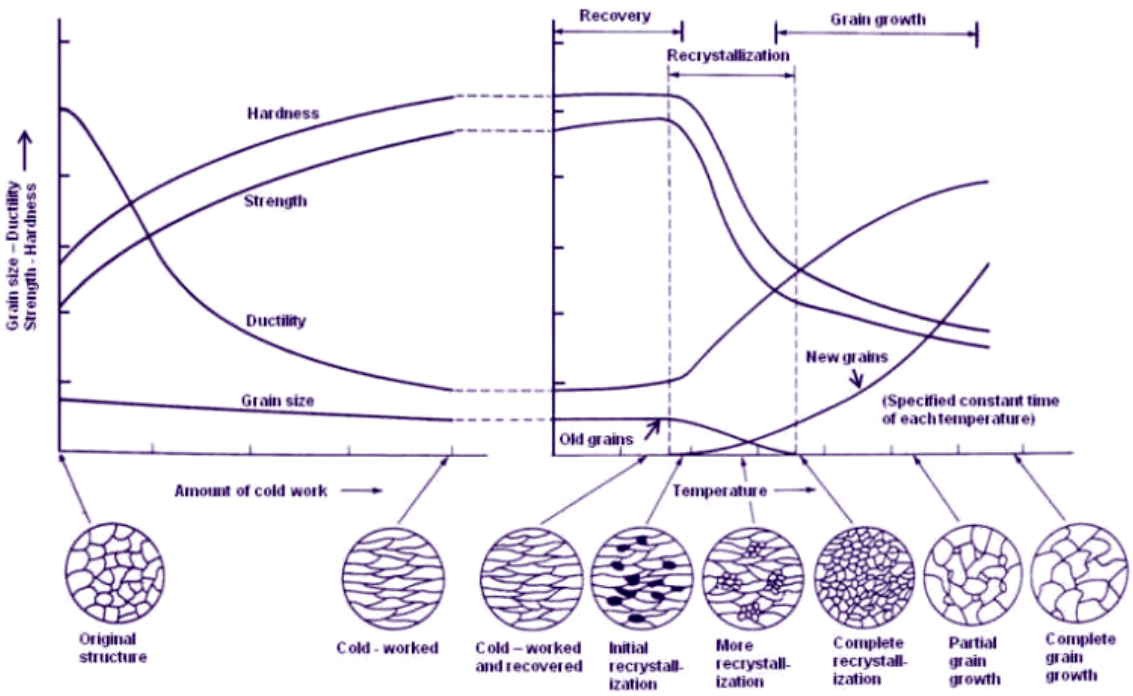



Figure 1.37: Effects of heat on structures and properties of cold worked steel.

### 1.9.1.3 Stress Relief Annealing

Stress Relieving annealing is applied to both ferrous and nonferrous alloys and is intended to remove internal residual stresses generated by prior manufacturing processes such as large casting, machining, cold rolling, welding, etc, Fig.1.38

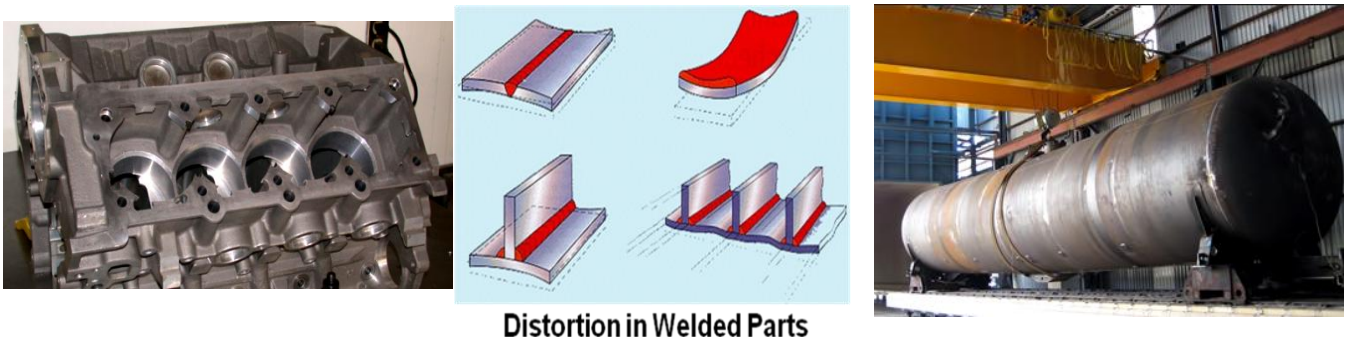



Figure 1.38: Various components that need stress relieve annealing.

Without stress relief annealing of these products, subsequent processing may give rise to unacceptable distortion and/or the material can suffer from service problems such as stress corrosion cracking. The treatment is not intended to produce significant changes in material microstructures as well as in mechanical properties and is, therefore, normally restricted to relatively low temperatures. Carbon steels and alloy steels can be given two forms of stress relief: (1) treatment at typically 150-200°C relieves peak stresses after hardening without significantly reducing hardness (e.g. case hardened components, bearings, etc.), (2) treatment at typically 600-750°C (e.g. after welding, machining, alloy steel casting etc.) provides virtually complete stress relief.

Cold worked austenitic stainless steels will contain some 'strain induced' martensite, which, makes the steel partially 'ferro-magnetic'. This can also reduce the corrosion resistance of the austenitic stainless steel. A highly stressed cold worked structure may also have lower general corrosion resistance than a fully softened austenitic structure, Fig.1.39.

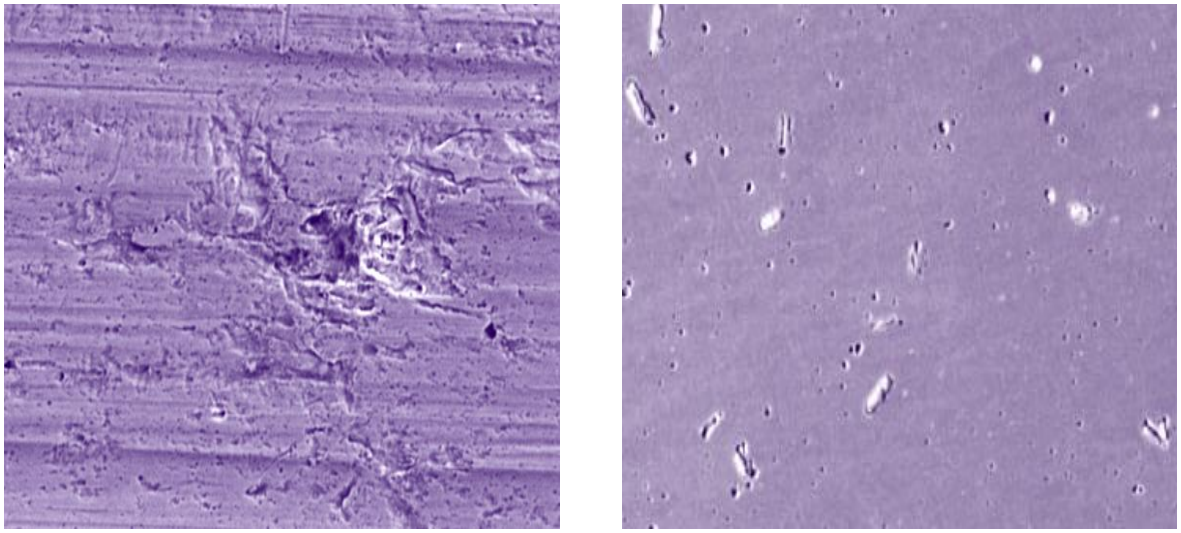


Figure 1.39: Corrosion behaviours of cold worked austenitic stainless steel before (left) and after (right) stress relief annealing.

The main hazard is stress corrosion cracking (SCC), which relies on tensile stresses as part of the failure mechanism. Stress relieving removes such residual tensile stresses and so improves the SCC resistance. Austenitic stainless steels are stress relieved below 480°C or above 900°C, temperatures in between reducing corrosion resistance in grades that are not stabilized or low carbon. Treatments above 900°C are often full solution annealing. The other main reason for stress relieving is to provide dimensional or shape stability. The risk of distortion can be reduced during forming or machining operations by stress relieving. Nonferrous alloys are stress relieved at a wide variety of temperatures related to alloy type and condition. Alloys that have been age hardened are restricted to stress relieving temperatures below the ageing temperature.

### 1.9.1.4 Spheroidizing

Cast high carbon or medium (Fig.1.40, top left) and high carbon steels having a microstructure containing even coarse pearlite (top middle and right) may still be too hard to conveniently machine or plastically deform. These steels, and in fact any steel, may be heat treated or annealed to develop the spheroidite structure. Spheroidized steels have a maximum softness and ductility and are easily machined or deformed. The spheroidizing heat treatment, during which there is a coalescence of the $Fe_3C$ to form the spheroid particles, Fig.1.40 (bottom).

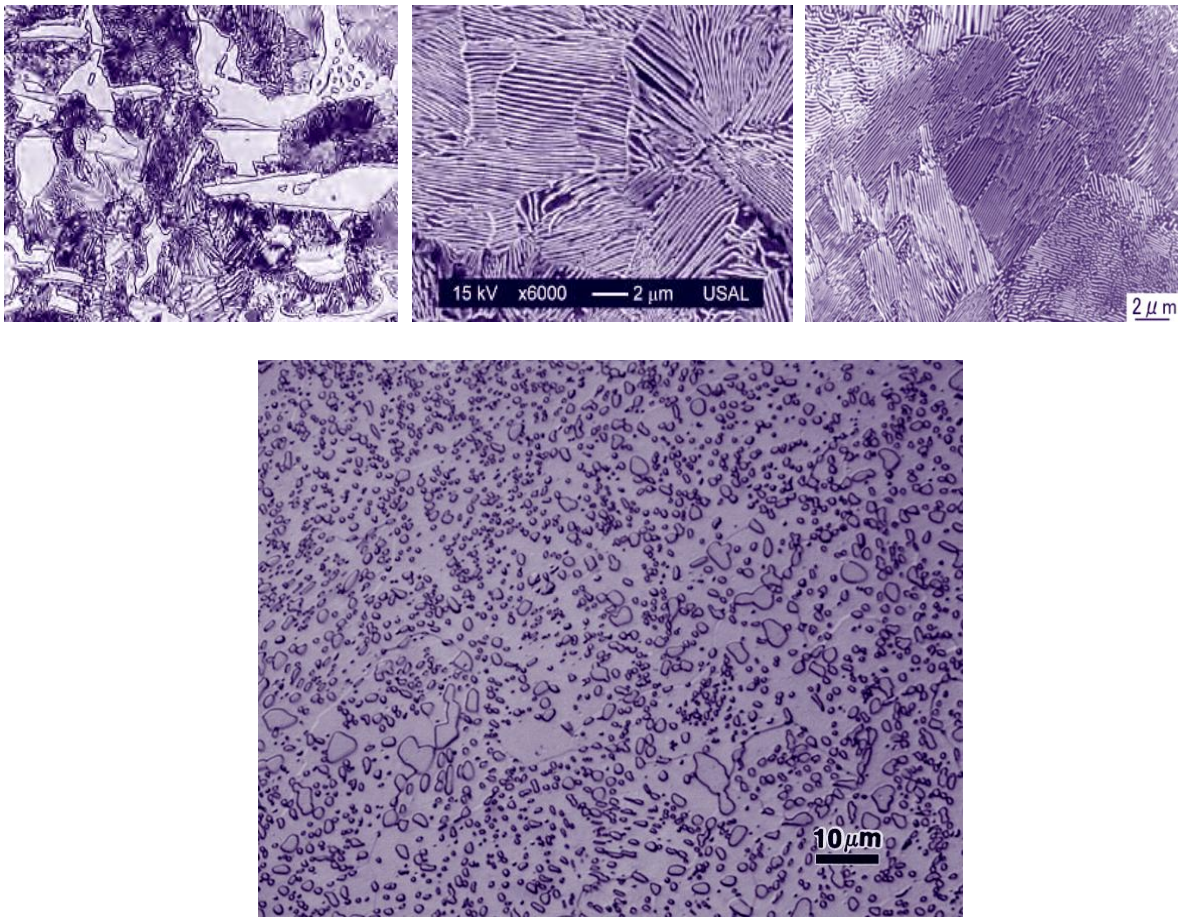



Figure 1.40: Microstructures of high carbon alloy cast steel (top left), eutectoid steels with coarse pearlite (top middle, right one is fine pearlite) and spheroidized high carbon steel (bottom).

Spheroidizing heat treatment can be carried out in several ways as follows:

- Heating the alloy at a temperature just below the eutectoid line (lower critical line) in the region of the Fe-C phase diagram. If the precursor microstructure contains pearlite, spheroidizing times will ordinarily range between 15 and 25 h.
- Heating to a temperature just above the eutectoid temperature and then either cooling very slowly in the furnace, or holding at a temperature just below the eutectoid temperature.
- Heating and cooling alternately within about of the eutectoid line.

Spheroidizing annealing is usually used for high carbon steels (carbon>0.6%). To some degree, the rate at which spheroidite forms depends on prior microstructure. For example, it is slowest for coarse pearlite and with the fineness of pearlite grains the spheroidization rate increases. Also, prior cold work increases the spheroidizing reaction rate. Various spheroidizing heat treatment cycles that used generally used are shown in the following Fig.1.41.

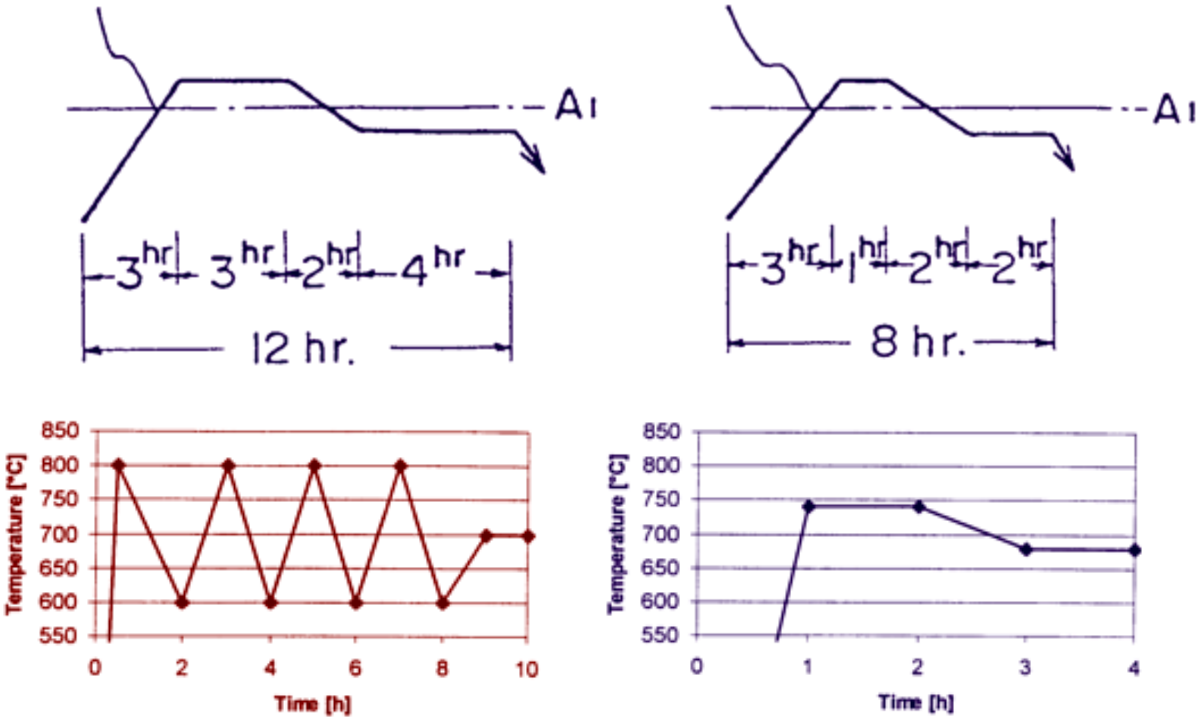



Figure 1.41: Various types spheroidizing heat treatment cycles.

### 1.10 Normalizing

Normalizing is a heat treatment process, which is accomplished by heating at least 50-60$^{o}$C above the upper critical temperature (Fig.1.42) for all steels and after soaking at the normalizing temperature for specific time period, the object is then cooled in the still air. The soaking time should be chosen properly so that the alloy is completely transformed to austenite.

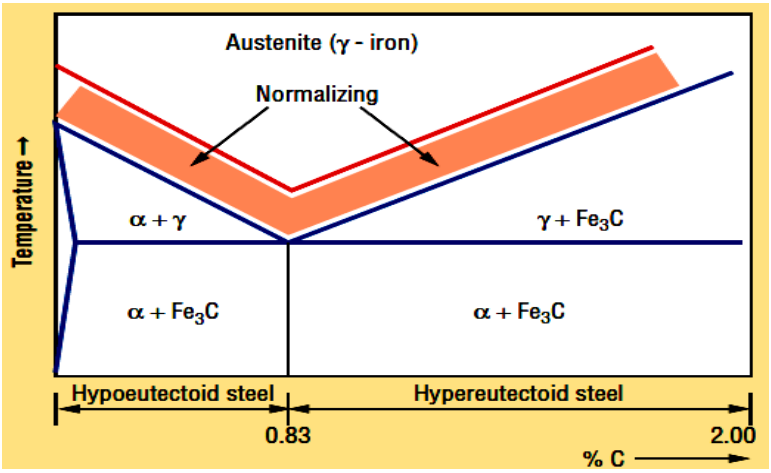



Figure 1.42: Temperatures for normalizing heat treatment.

Here it is to be mentioned that there two upper critical temperature lines in the iron carbon diagram as $A_3$ and $A_{cm}$. For normalizing, temperatures above uppercritical lines are to be used, which are different for hypoeutectoid and hypereutectoidsteels. In the case of hypoeutectoid steels, the uppercritical temperature is similar to that used for calculation in anneaing. However, for hypereutectoid steel, it is significantly different, which can be calculated using the following relationship:

$$A_{cm} = 224 + 992C - 465C^2 + 7.5Mn + 16Si + 47Cr + 10Mo - 7Ni$$

Soaking periods for normalizing are typically one hour per inch of cross sectional area, but not less than two hours holding at the austenitizing temperature. It is important to remember that the mass of the part or the work load can have a significant influence on the cooling rate and thus on the resulting microstructure. Thin pieces cool faster and are harder after normalizing than thicker ones. By contrast, after furnace cooling in an annealing process, the hardness of the thin and thicker sections will be of almost similar. Normalizing heat treatment, compared to annealing, provides better hardness and strength to iron and steel components. However, the resulted strength is significantly lower than the quenched or quenched and tempered steel, Fig.1.43 In addition, normalizing helps reduce internal stresses induced by such operations as forging, casting, machining, forming or welding.

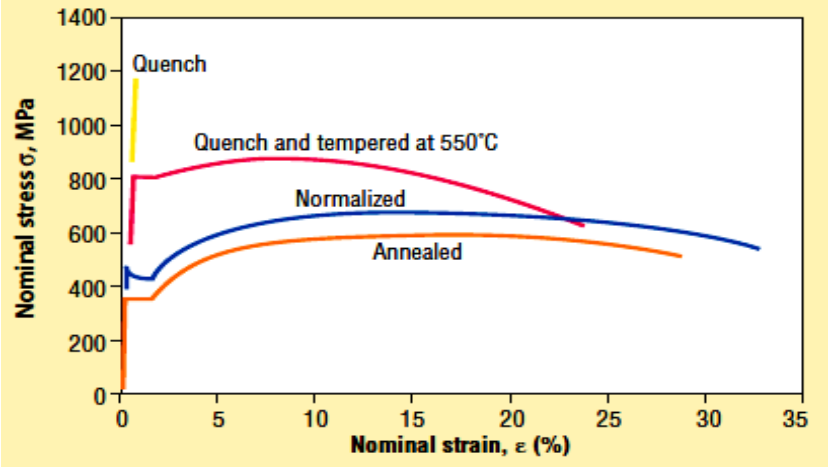



Figure 1.43: Comparison of tensile strength of quenched and tempered, normalized and annealed mild steels.

Normalizing also improves microstructural homogeneity and response to heat treatment (e.g. annealing or hardening) and enhances stability for subsequent lower temperature processes. Parts that require maximum toughness and those subjected to impact are often normalized. When large cross sections are normalized, they are also tempered to further reduce stress and more closely control mechanical properties. Normalizing is typically performed in order to:

(a) Improve machinability

(b) Improve dimensional stability
(c) Modify and/or refine the grain structure
(d) Produce a homogeneous microstructure
(e) Reduce banding
(f) Improve ductility
(g) Provide a more consistent response when hardening or case hardening

By way of example, many gear blanks are normalized prior to machining so that during subsequent hardening or case hardening dimensional changes such as growth, shrinkage or warpage will be better controlled. It is important to remember that the mass of the part or the workload can have a significant influence on the cooling rate and thus on the resulting microstructure. Thin pieces cool faster and are harder after normalizing than thicker ones. By contrast, after furnace cooling in an annealing process, the hardness values of the thin and thicker sections are about the same.

Castings with relatively nonuniform wall thickness and section sizes are usually annealed rather than normalized. Other castings, especially those having a complex shape or interconnected thick and thin sections and are thus prone to high levels of residual stresses, benefit from normalizing. The microstructure obtained by normalizing depends on the composition of the castings (which dictates its hardenability) and the cooling rate. Normalizing also improves microstructural homogeneity and refines the grain sizes. This type of grain refinement also contributes in strengthening the steel. As a result, in general, normalized steel a fixed chemical composition is stronger than that in the annealed condition. In the following Fig.1.44, the refinement of microstructures of a carbon steel having 0.4%C is shown.

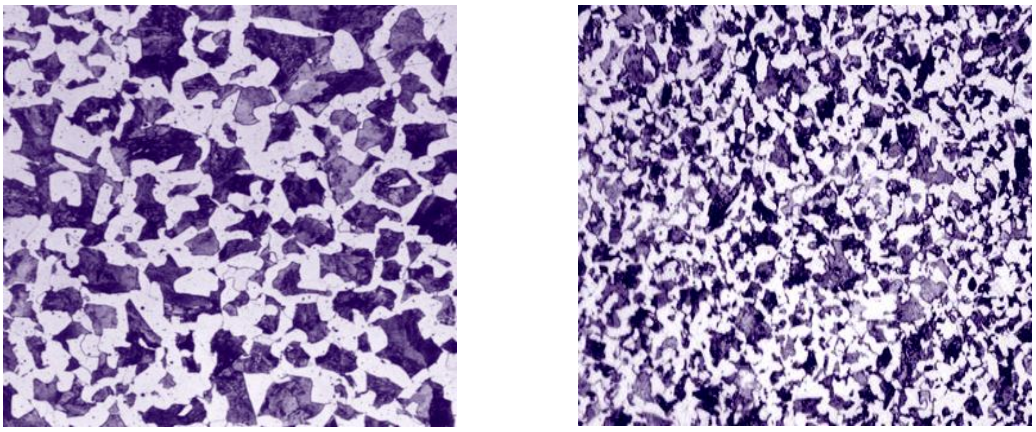


Figure 1.44: Microstructures of annealed (left) and normalized (right) 0.4%C steel.

In hypereutectoid steel annealing treatment, in general, results thick and continuous cementite network, which is not good for machining. On the other hand, network type cementite tremendously reduces the tensile strength and toughness of the steel because of a very poor tensile strength of the cementite phase (about 5000psi). For this type of steel, normalizing breaks

down the continuity of the cementite networks and induces higher strength as well as toughness, Fig.1.45.

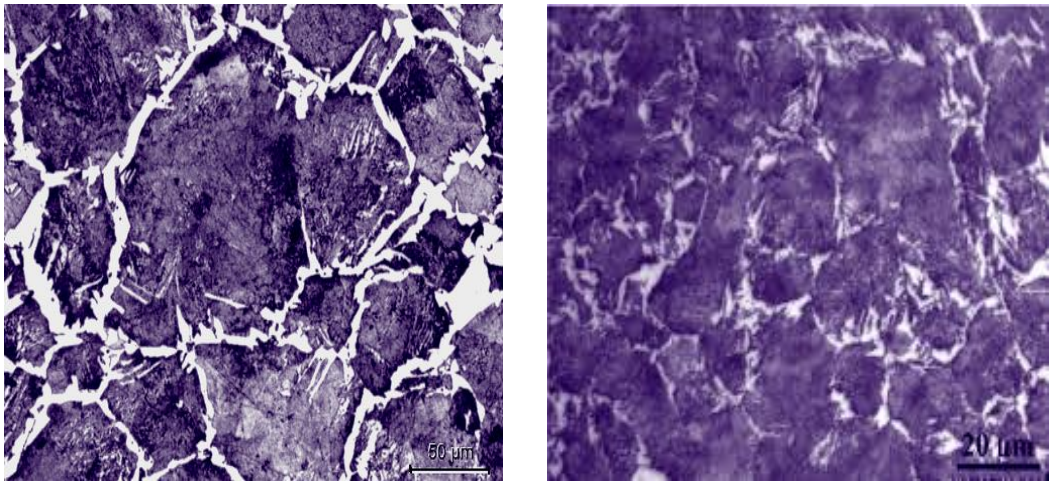



Figure 1.45: Microstructures of annealed (left) and normalized (right) hypereutectoid steel.

Another important difference in heat treatment parameter of normalizing and annealing is the temperature selection for hypereutectoid steel as seen in the diagram, which is above the upper critical temperature for normalizing, whereas, it is above lower critical temperature for annealing. The main reason behind this is that annealing is usually performed as an intermediate heat treatment to make the subsequent operations as machining, homogenization of chemical compositions, removal residual stress, etc easy. Annealing at just above the lower critical temperature provide the necessary solution. As normalizing is a final heat treatment, normalizing above lower critical temperature makes the product soft. On the other hand normalizing at this temperature might also form network type cementite, which is not beneficial for any load bearing component as network type cementite deteriorates both the strength and ductility of hypereutectoid steels. After hot rolling, the structure of steel is usually oriented in the rolling direction. To remove the oriented structure and obtain the same mechanical properties in all directions, a normalizing has to be performed, Fig.1.46.

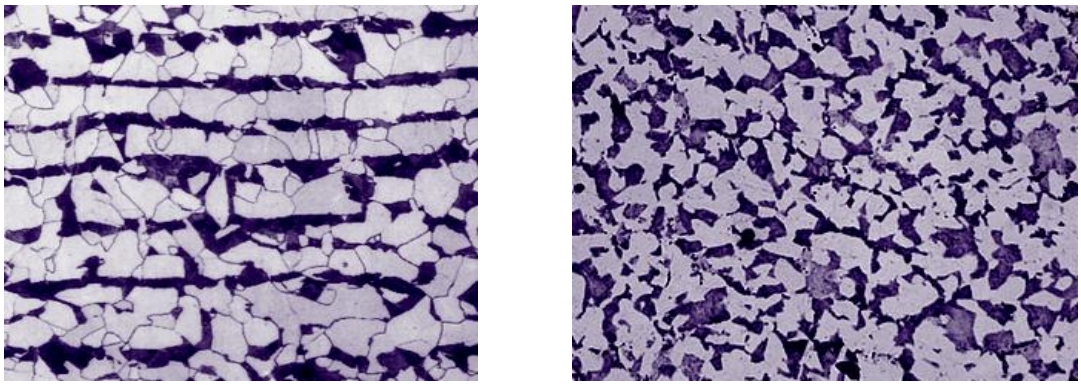


Figure 1.46: Normalizing heat treatment reduces aligned pearlite and also refines the ferrite-pearlite grains.

Normalizing treatment results a better combination of mechanical properties. At lower carbon level, annealing and normalizing do not present a significant difference on the mechanical properties like tensile strength, yield strength, ductility and toughness of steels. However, as the carbon content increases, however, the difference increases especially for strength, Fig.1.47. For ductility, the difference still not so significant. Another important observation is that when the carbon content is significantly above the eutectoid carbon content (0.80%), the toughness gradually recovers and above 0.9% carbon it becomes better for normalized steel. Because, normalizing heat treatment helps break the cementite network around the pearlite grains.

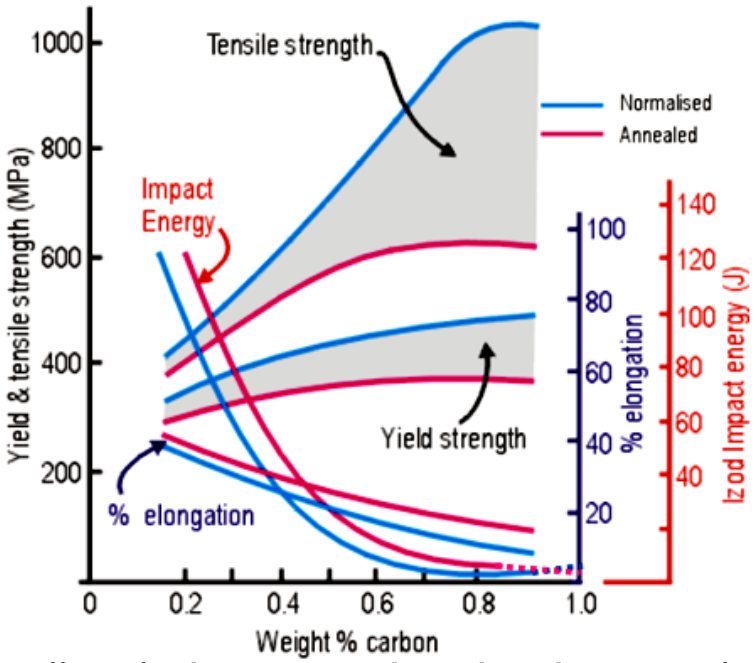



Figure 1.47: Effects of carbon content on the mechanical properties of annealed and normalized carbon steels.

Improper austenitizing temperature will not make homogenization in carbon content, so after cooling, the distribution of ferrite and pearlite will also be inhomogeneous, Fig.1.48.

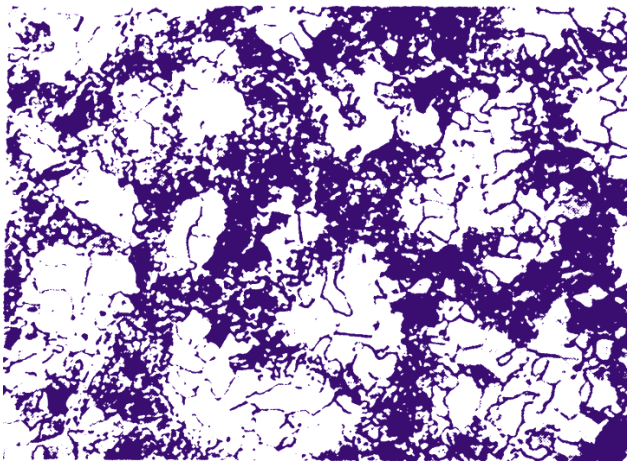


Figure 1.48: Inhomogeneous ferrite and pearlite in normalized carbon steel because of improper normalizing temperature.

During austenitizing a far reaching dissolution of carbides is aimed at, but this process competes with the growth of austenite grains after complete carbide dissolution, which is not desirable. Besides the carbide dissolution, the degree of homogenization within the austenite matrix is important for obtaining a new arrangement of ferrite and pearlite constituents in the structure after normalizing. Both dissolution and homogenizing are time and temperature dependent diffusion processes that are slower when the diffusion paths are longer (higher local differences in carbon concentration) and the diffusion rates are smaller (e.g., increasing amounts of alloying elements). Therefore, especially with alloyed steels, lower austenitizing temperatures and longer holding times for normalizing give advantages taking into account the austenite grain growth. High austenitizing temperatures result in a coarse grained austenite structure, which yields a coarse structure after normalizing. Holding time at austenitizing temperature may be calculated using the empirical formula:

$$T = 60 + D$$

where T is the holding time (min) and D is the maximum diameter of the workpiece (mm).

**Problem 1.4:** Design the annealing and normalizing schedules for 1020, 1040, 1080, 4140 and 4340 steel bars having 40mm diameter. Also calculate the UTS, YS and %elongation of the annealed and normalized steels.

**Solutions:** Self.

### 1.11 Hardening of Steels

Hardening is a process of heating the steel component to a sufficiently high temperature (in the austenite zone), holding there for specific time and then cooling at such a rate that enables to avoid the formation of normal ferrite and/or pearlite phases and causes formation of metastable martensitic structure in the steels so that a significant increase in hardness occurs. In most cases, hardening is performed in connection with a subsequent new heating, the tempering. If, after hardening at a high temperature, tempering is performed and then a relatively low hardness combined with high toughness is achieved, which is called hardening and tempering.

#### 1.11.1 How Does Hardening Take Place?

The hardening process of workpieces can be divided into three technical steps. First, the workpiece is heated so that the input structure transforms to an austenitic structure. This austenitizing temperature depends on the material used (750-1210°C). Then the workpiece is maintained at this temperature so that alloying elements can be incorporated homogenously in this austenitic structure. The final step is quenching the workpiece at such a cooling rate that a so called martensitic structure is originated. The cooling rate at which austenite, from surface to the core, is transformed to martensite is called the critical cooling rate.

The heating rate and temperature should be selected properly and maintained in a protective atmosphere to protect the material from oxidation and decarburization. Cooling can be performed in different media. The most common are: water, saline water (brine), hardening oils, polymers, salt bath, nitrogen or argon, etc. After hardening steel has a relatively high brittleness, therefore, directly after hardening it must be tempered at least once, however, more times is better.

### 1.11.2 The Theory Behind Hardening

Steel has in an unhardened state (A in Fig.1.49) a body centered cubic (BCC) structure, in which it can only dissolve very little carbon although it has a 32% empty space in BCC cell. After warming up over approximately 720°C austenite is originated that has a face centered (FCC; B) crystal structure (and occupies relatively a smaller volume). It can dissolve considerably more carbon because of absence of central atom (even though the empty space is only 26% in the cell), which occurs at hardening temperature. By cooling the material then rapidly enough, converting it from a cubic face centered crystal structure back into a cubic spatially centered structure where oversaturated carbon remains inside the cell and martensite is originated. Due to the presence of supersaturated carbon, the BCC lattice is stretched out to a body centered tetragonal lattice (C) called martensite, Fig.1.50. The martensite thus possesses high internal stresses and a larger volume than nonhardened steel at room temperature. As a consequence, the high internal stresses have a high hardness of the material. Upon tempering, a little carbon will be diffused from the tetragonal cube, which is called tempered martensite.

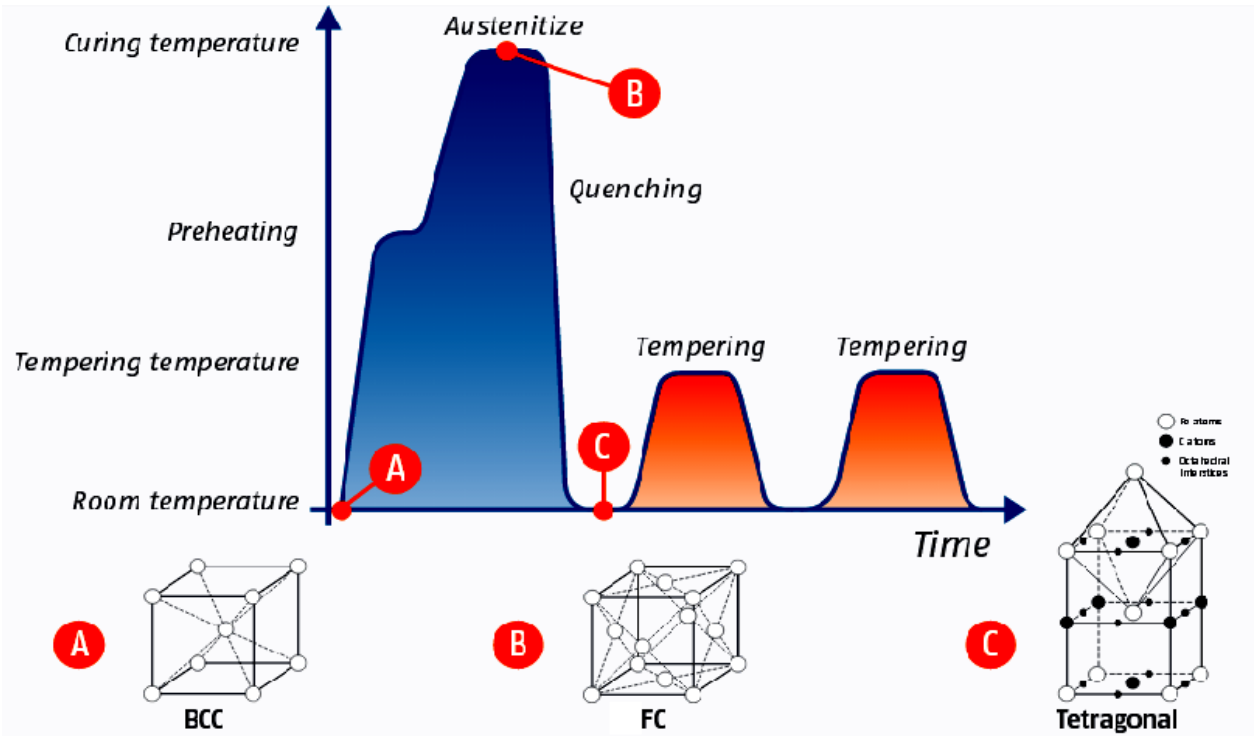



Figure 1.49: Heating and cooling cycles for hardening and subsequent changes in the crystallographic structures.

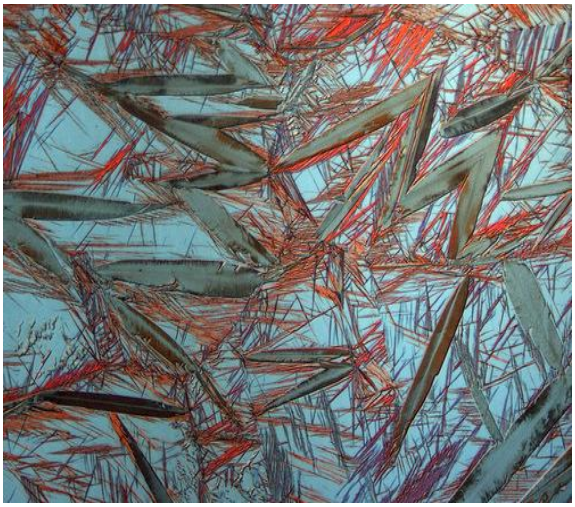


Figure 1.50: Micrograph showing the as quenched martensitic microstructures.

For proper and uniform hardening, the steel should be austenitized homogeneously. Here heating rate, temperature selection and holding time are very important parameter to be controlled preciously.

### 1.11.3 Austenitizing

Austenitizing is the first operation in hardening heat treatment processes on which the properties of the hardened parts mostly depend. The austenitizing temperature for hardening is very similar to that of the full annealing. However, the selection of temperature and soaking time should be more precise and needs more care as it is the final heat treatment process and that the hardened components are usually used for more critical applications.

### 1.11.4 Metallurgical Aspects of Austenitizing

The way of austenite formation in a certain steel on heating depends very much on the starting microstructures of the selected steel. Equalizing of the carbon concentration proceeds gradually by diffusion, resulting in a homogeneous austenite structure at the end of this process. The holding time at austenitizing temperature required for this process is called the homogenization time. During pearlite to austenite transformation, several austenite grains are formed from one pearlite grain, i.e., the newly formed austenite is fine grained. For hypoeutectoid steel, the microstructure is composed of ferrite and pearlite. In pearlitic (Fig.1.51a) structures it starts primarily at the intersection of pearlite colonies but also at cementite lamellae. In the case of spheroidized structures nucleation starts on carbide particles (b), austenite formation starts from carbide surface. For ferritic structures the nucleation sites are situated primarily at grain boundaries (c).

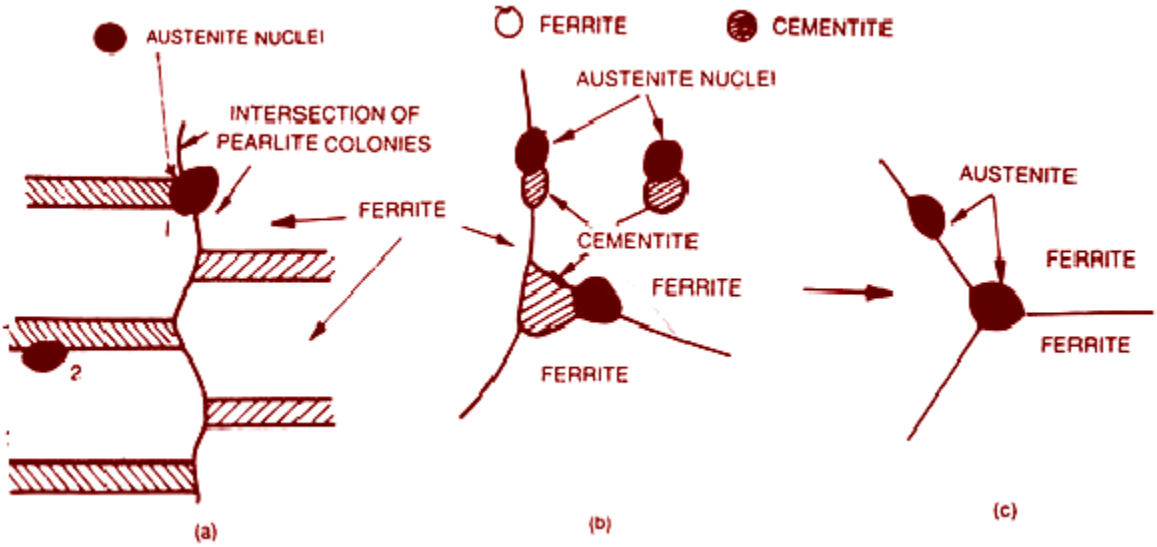



Figure 1.51: Austenite nuclei formation sites during austenitization of steels having various microstructural morphologies.

At the austenitization temperature, austenite does not form instantly. From the beginning of austenitization a certain incubation time is necessary to form the first nuclei and then the process proceeds at a more rapid rate as more nuclei develop and grow. At higher temperatures the diffusion rate increases and austenite forms more rapidly, Fig.1.52.

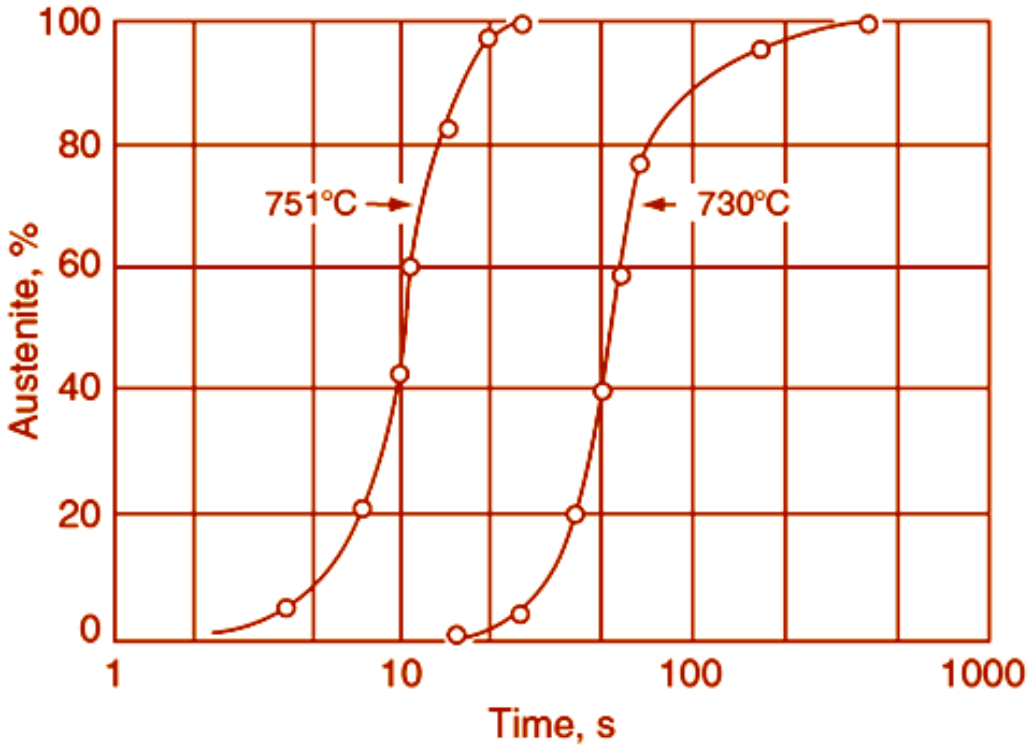



Figure 1.52: Effects of austenitization temperature on the incubation period of austenite formation and its growth in a typical eutectoid steel.

From above Fig.1.52 (for eutectoid carbon steel of 0.8% C), one can see that if an austenitizing temperature of 730$^{o}$C is maintained (after a rapid heating ), the transformation will start in about 30s. If instead an austenitizing temperature of 750$^{o}$C is chosen, the transformation will begin in 10s and finish within 50s. However, if the steel is to be fully austenitic along with dissolution of all carbides, it must be held at this temperature for a long period of time.

### 1.11.5 Heating Rate

The technologically allowed heating rate is the maximum heating rate that can be applied in actual circumstances, taking into account the fact that thermal stresses that develop within the workpiece must not exceed the critical value. Because this could cause warping or cracking, since sections having different dimensions heat up at different speeds and large temperature gradients can arise between the surface and the core of the workpiece. In the practical situations, this heating rate depends on:

a) The mass and shape of the workpiece (the ratio between its volume and surface area)
b) The chemical composition of the material
c) The initial microstructures

When workpieces of heavy sections or of complicated shapes are heated, temperatures between 250 and 600$^{o}$C are particularly dangerous, because in this temperature range the steel does not have enough plasticity to compensate for thermal stresses. If the heating of an object is asymmetrical, the object will warp. If thermal stresses are developed that overstep the strength of the material (which is substantially lower at higher temperatures), cracks will result. If the heating rate is too high through the transformation temperature range (between $A_1$ and $A_3$), warping may occur because of volume change of the structure lattice. The tendency of a steel to crack during heating depends on its chemical compositions. We know that steel is an alloy of iron and carbon. However, intentionally or by other means, the chemical compositions of any steel is not so simple. So, the interaction of the elements with each other is not so straight forward. The complex interaction of carbon and other alloying elements is expressed by the following empirical formula termed the carbon equivalent:

$$\mathbf{CE} = \frac{C + \mathrm{Mn}}{5} + \frac{\mathrm{Cr}}{4} + \frac{\mathrm{Mo}}{3} + \frac{\mathrm{Ni}}{10} + \frac{\mathrm{V}}{5} + \frac{\mathrm{Si} - 0.5}{5} + \frac{\mathrm{Ti}}{5} + \frac{\mathrm{W}}{10} + \frac{\mathrm{Al}}{10}$$

where the element symbols represent wt% content. This formula is valid up to the following the maximum values of alloying elements.

| | |
|---|---|
| $C \leq 0.9\%$ | $V \leq 0.25\%$ |
| $Mn \leq 1.1\%$ | $Si \leq 1.8\%$ |
| $Cr \leq 1.8\%$ | $Ti \leq 0.5\%$ |
| $Mo \leq 0.5\%$ | $W \leq 2.0\%$ |
| $Ni \leq 5.0\%$ | $Al \leq 2.0\%$ |

The values of the alloying elements actually present are put into the formula in wt%. The higher the calculated CE value, the greater is the sensitivity of the steel to cracking. For safe heat treatment operation, the following information might be very helpful.

CE ≤ 0.4: The steel is not sensitive to cracking (it may be heated quite rapidly).
CE = 0.4–0.7: The steel is medium sensitive to cracking.
CE ≥ 0.7: The steel is very sensitive to cracking (when heating up a preheating operation should be included).

During austenitization for hardening, the heating rate is very important because full austenitization is required for uniform hardening, which is heating rate sensitive, which has been explained in Fig.153.

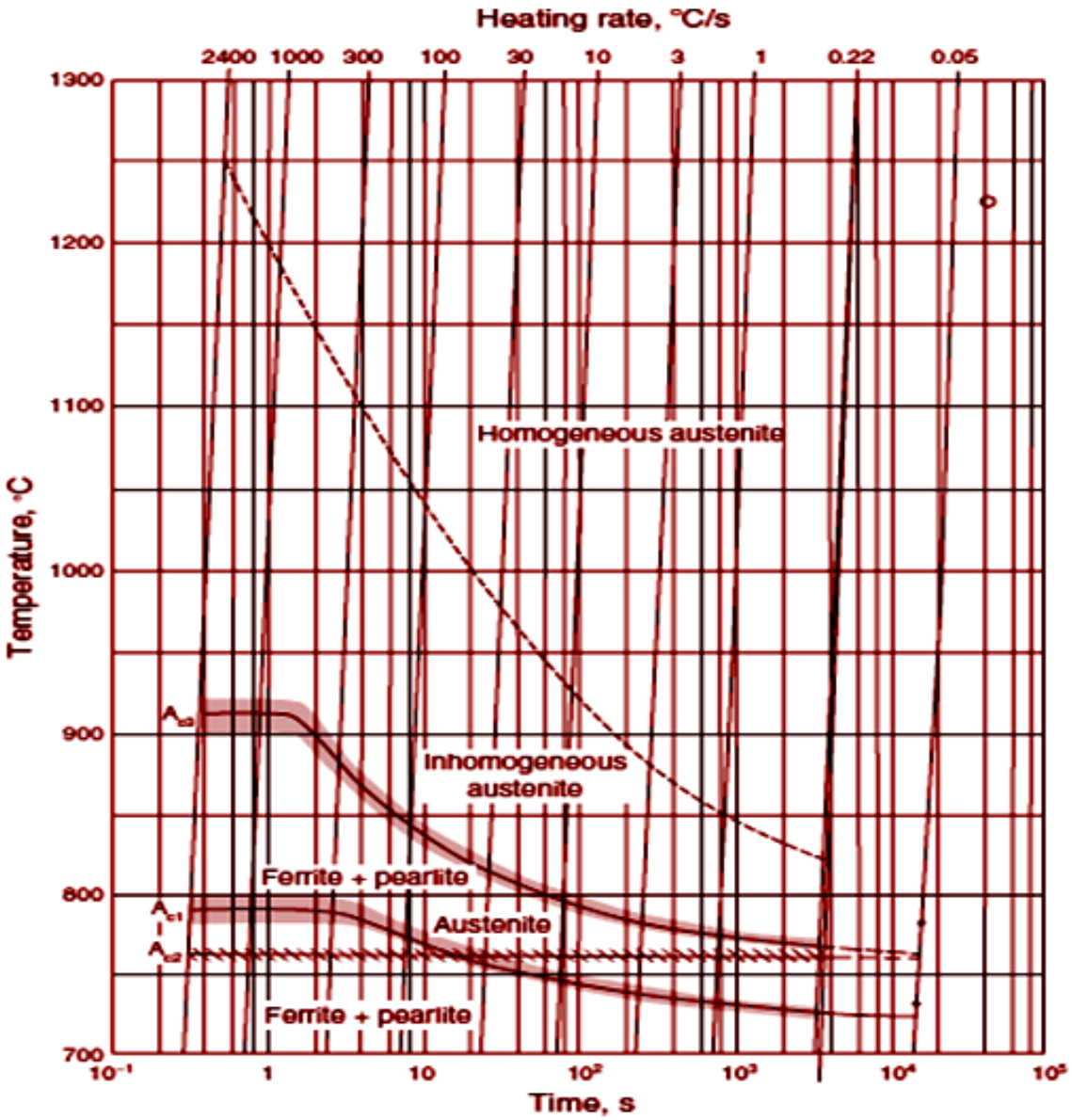



Figure 1.53: Effects of heating rate on the transformation and homogenization of austenite in steels.

If the heating rate is extremely slow (e.g., 0.22°C/s, Fig.1.53 below) to about 775°C, on crossing the $A_3$ temperature after about 1h all pearlite and ferrite would be transformed to inhomogeneous austenite. At a heating rate of 10°C/s the pearlite and ferrite would have been transformed to inhomogeneous austenite after crossing the $A_3$ temperature at about 800°C after only 80s. A remarkable feature of such diagrams is that they show precisely the increase of $Ac_1$ and $A_3$ transformation temperatures with increasing heating rates. This is especially important when short time heating processes like induction hardening or laser beam hardening, with heating rates ranging to about 1000°C/s, are applied for surface hardening. In such a case this diagram should be consulted to determine the required austenitizing temperature, which is much higher than in conventional hardening of the same grade of steel. For the steel in question, for example, the conventional hardening temperature would be in the range of 830–850°C, but for induction or laser beam hardening processes the hardening temperatures required are between 950 and 1000°C. When heating at a rate of 1000°C/s to the austenitizing temperature of 1000°C, only 1 s is necessary, and the above mentioned short heating time processes operate in approximately this time range. However, for quality heat treatment this diagram is equally important.

**Problem 1.5**: Design the heat treatment schedules for hardening of AISI 1040, 4340 and 8620 grade of steels.

**Solution**: (1) Identify the chemical compositions of the selected steels, (2) calculate the CE value, take decision concerning the heating rate and whether reheating essential or not, consult with Fig.1.53 to find out the heating rate required for austenite transformation and equalization.

As per the above Fig.1.53, much higher temperatures are necessary to achieve the homogeneous austenite structure. In such a case one is, of course, concerned with the grain growth. On the other hand, if the austenite homogenization is not proper hardening will not be perfect, Fig.1.54. At the same time, excessive grain growth will also result inferior quality of hardening. So, there must be balanced parameter selection for good hardening practice, although it's a very tricky job.

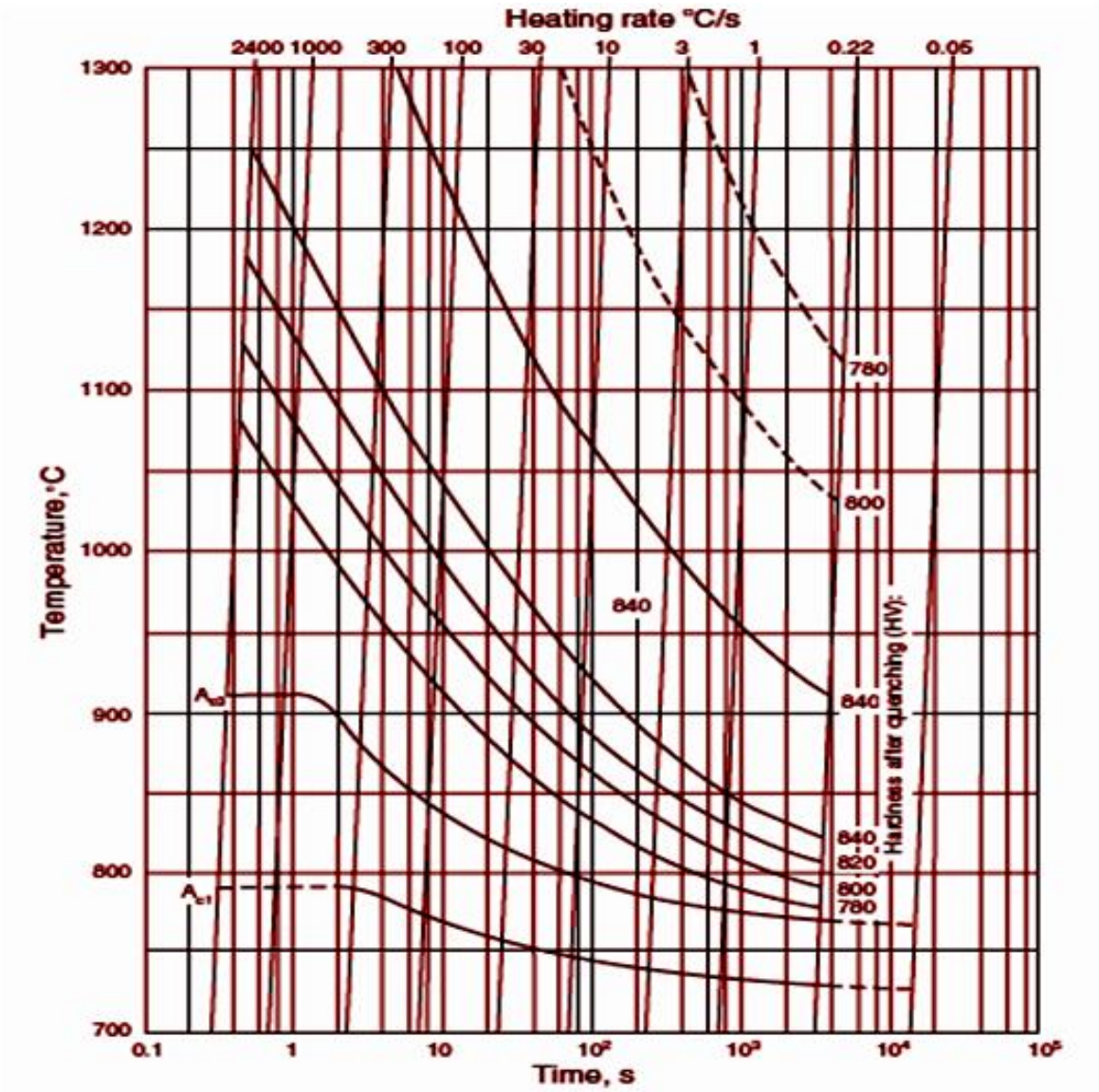



Figure 1.54: Effects of heating rate and austenitization temperature on the hardness of hardened steels.

For eutectoid and hypereutectoid steel grades, which after quenching develop substantial amounts of retained austenite, the attainment of maximum hardness after quenching is more complicated. For DIN 100Cr6 steel (1.0% C, 0.22% Si, 0.24% Mn, and 1.52% Cr), the maximum hardness of 900 HV after quenching is attained on heating to a very narrow temperature range, and furthermore this temperature range is displaced toward higher temperatures as the heating rate is increased. If this steel is quenched from temperatures that exceed the optimum range, the resulting hardness is reduced owing the presence of an increasing amount of retained austenite.

**Problem 1.6**: Design the heat treatment schedules for hardening of AISI 1040, 1060 and 1080 steels where the target is to achieve hardness value of around 700HV.

**Solution**: Similar to previous one, but additionally consultation of with Fig.54 is required.

### 1.11.6 Quenching

After fully austenitization, the next step is to quench the heated component in proper cooling media to achieve martensitic structures. There two different ways to transform the austenite to martensite; namely: isothermal cooling and continuous cooling transformation.

#### 1.11.6.1 Isothermal Transformation Diagrams

To understand the kinetics of transformations to austenite, it is important to follow the process at a constant temperature. For this, a diagram has been constructed that characterizes the isothermal process of austenite transformation to other phases like pearlite, bainite and martensite. In this diagram, the transformation time is the abscissa on the logarithmic scale and the temperature is plotted on the ordinate, Fig.1.55.

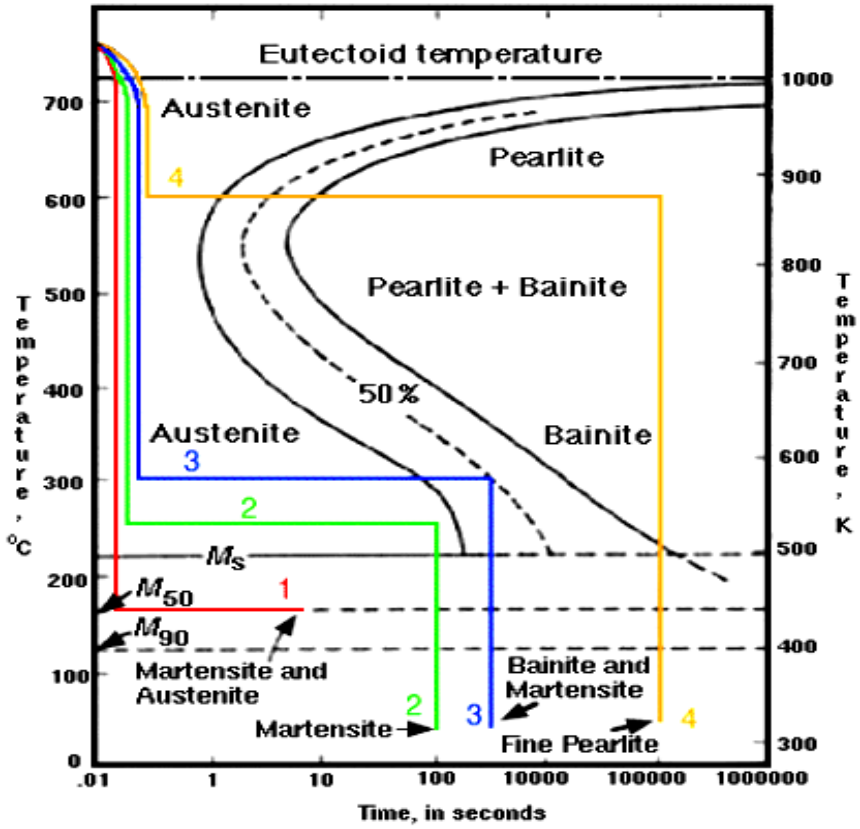



Figure 1.55: Isothermal temperature transformation (ITT) diagram of a typical eutectoid steel.

From the above diagram, the incubation period (left most line of the S shaped curve) can be determined and also the time required for completion of the process (right most line of the curve). The instant an alloy passes the points A3 and A1 during quenching is usually taken as the zero time reference. The time required to achieve the temperature of the quenching medium is often neglected. The start and finish of the transformation are difficult to determine from the transformation curve behaviour at the initial and final sections of the curve. Therefore, the lines

of the ITT diagram usually correspond to a certain final volume that underwent transformation, e.g., 3 and 97% for the transformation start and finish, respectively.

In addition to the above mentioned curves, the diagram often contains intermediate curves that correspond to certain values of the transformed volume, e.g., 10, 50 (mid dotted line), or 90%. A decrease in the transformation rate causes displacement of the transformation start and finish curves to the right, i.e., toward greater duration. There are various options to delay the austenite transformation. For any particular steel, this phenomenon can be observed if it is possible to decrease in the number of foreign inclusions, carbide particles, enlargement of austenite grains and so on.

An increase in the transformation rate leads to displacement of the ITT curves to the left. This phenomenon can be accounted for by a decrease in the quenching heating temperature, the presence of carbides or foreign inclusions, and refinement of the austenite grain. For a given steel, the temperature that corresponds to the maximum transformation rate (the so-called nose of the sigmoid curve) does not, as a rule, change significantly.

If the cooling rate is high, the formation rate of separate needles of martensite is also high and transformation of austenite to martensite commences on reaching $M_s$. It continues on subsequent cooling to lower temperatures. As the temperature of the quenching medium is lowered, the amount of formed martensite rises first rapidly and then slowly. With an increase in the quenching heating temperature (austenitization temperature), the transformation also shifts toward lower temperatures as more of the alloying elements are taken into solution, Fig.1.56. A certain amount of martensite may be formed during isothermal holding, but it is not high in carbon steels. Retained austenite is stabilized during isothermal holding. As a result, more martensite is formed during subsequent cooling. Formation of martensite is completed at the point $M_f$.

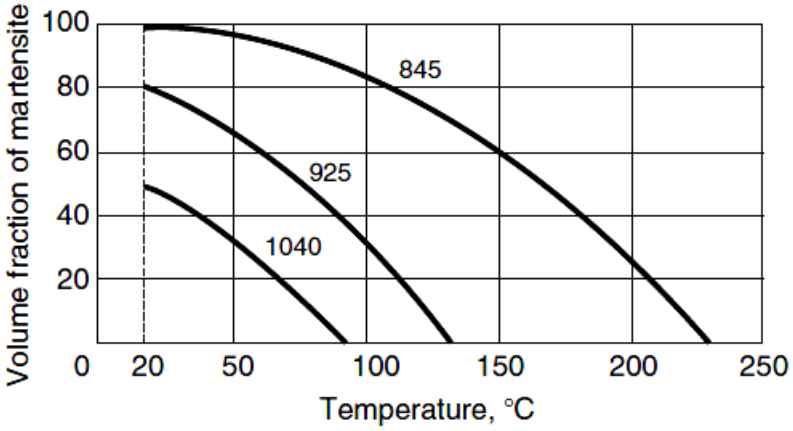



Figure 1.56: Effects of austenitization temperature on the quenching temperature and volume fraction of martensite formed for 0.4%C steel.

### 1.11.6.2 Continuous Cooling Transformation Diagrams

Isothermal heat treatments are not the most practical to conduct because an alloy must be rapidly cooled to and maintained at an elevated temperature from a higher temperature, which is really difficult as well as expensive. As a result, most heat treatments for steels involve the continuous cooling of a specimen to room temperature. For continuous cooling, the time required for a reaction to begin and end is delayed continuously with time. Thus the isothermal curves are shifted to longer times and lower temperatures, as indicated in Fig.1.57.

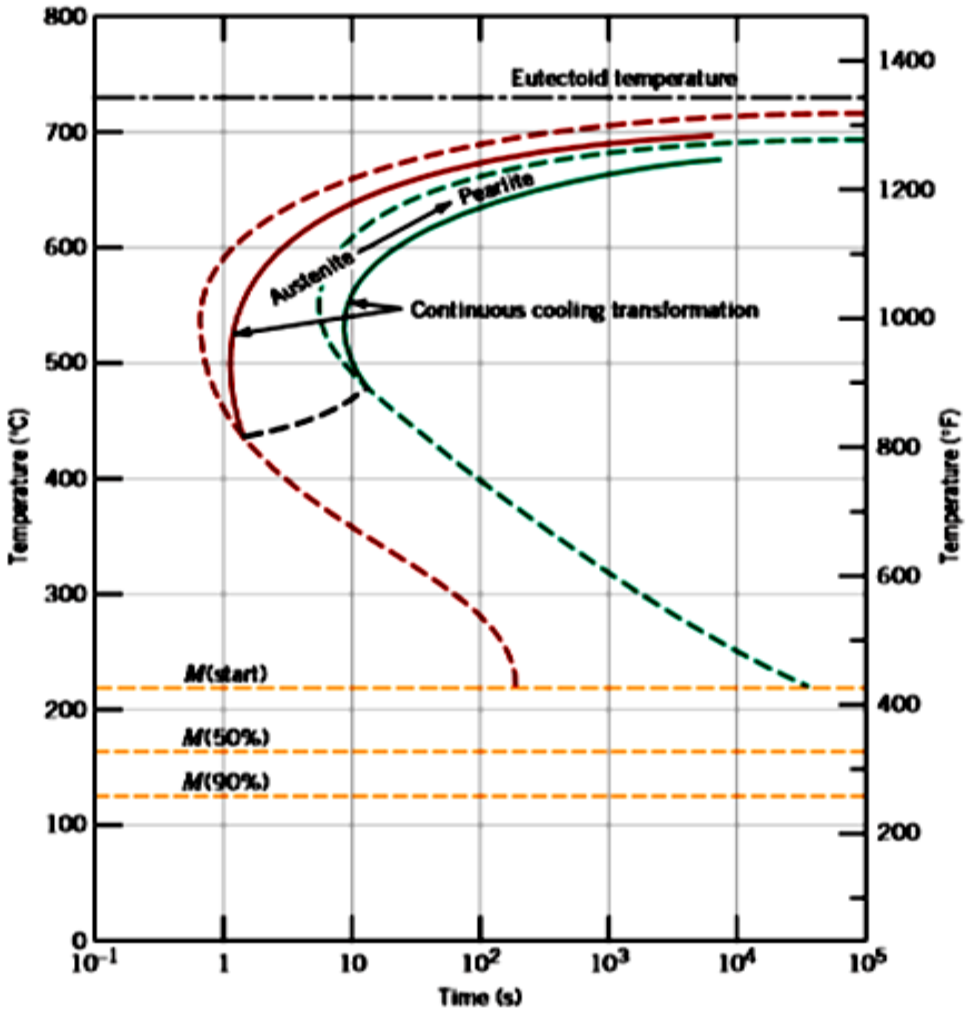



Figure 1.57: Continuous cooling transformation diagram for a typical eutectoid steel.

A plot containing such modified beginning and ending reaction curves is termed a continuous cooling transformation (CCT) diagram. Some control may be maintained over the rate of temperature change depending on the cooling environment. The transformation starts after a time period corresponding to the intersection of the cooling curve with the beginning reaction curve and concludes upon crossing the completion transformation curve. The microstructural products for the critical (fast) to slow cooling rate curves are shown in Fig.1.58.

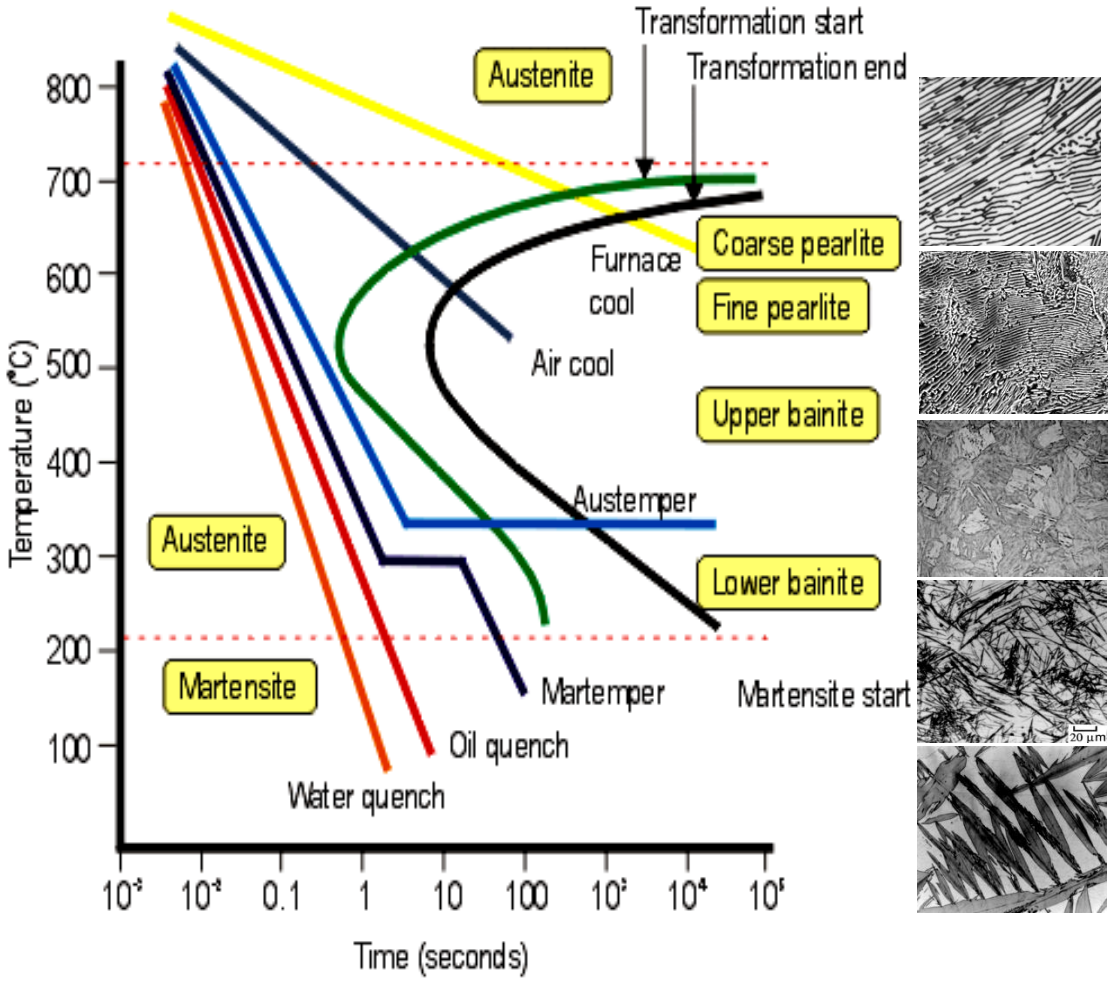



Figure 1.58: Continuous cooling transformation diagram for a typical eutectoid steel along with slow to fast cooling associated microstructures..

Normally, bainite will not form when an alloy of eutectoid composition or, for that matter, any plain carbon steel is continuously and slowly (furnace or air cooled) cooled to room temperature. This is because all the austenite will have transformed to pearlite by the time the bainite transformation has become possible. Thus, the region representing the austenite–pearlite transformation terminates just below the nose of the curve. For any cooling curve passing through the nose, the pearlitic or bainitic transformation ceases. With continued cooling, the unreacted austenite begins transforming to martensite upon crossing the M(start) line. So, depending on cooling rate and temperature below the M(start) temperature any percentage of martensite is possible to incorporate in the microstructures of the quenched steel through either isothermal and continuous cooling process.

For the continuous cooling of a steel alloy, there exists a critical quenching rate, which represents the minimum rate of quenching that will produce a totally martensitic structure. This critical cooling rate, when included on the continuous transformation diagram, will just miss the

nose at which the pearlite transformation begins. Finally, a totally pearlitic structure develops for low cooling rates. Carbon and other alloying elements also shift the pearlite (as well as the proeutectoid phase) and bainite noses to longer times, thus decreasing the critical cooling rate. In fact, one of the reasons for alloying steels is to facilitate the formation of martensite so that totally martensitic structures can develop in relatively thick cross sections. In fact, iron-carbon alloys containing less than about 0.25 wt% carbon are not normally heat treated to form martensite because quenching rates too rapid to be achieved through practically available cooling media. Other alloying elements that are particularly effective in rendering steels heat treatable are chromium, nickel, molybdenum, manganese, silicon, and tungsten; however, these elements must be in solid solution with the austenite at the time of quenching.

In summary, isothermal and continuous cooling transformation diagrams are, in a sense, phase diagrams in which the parameter of time is introduced. Each is experimentally determined for an alloy of specified composition, the variables being temperature and time. These diagrams allow prediction of the microstructure after some time period for constant temperature and continuous cooling heat treatments, respectively.

### 1.11.6.3 Retained Austenite and Cryogenic Treatment

The martensite start ($M_s$) and martensite finish ($M_f$) temperatures for unalloyed steels depend on their carbon content, Fig.1.59.

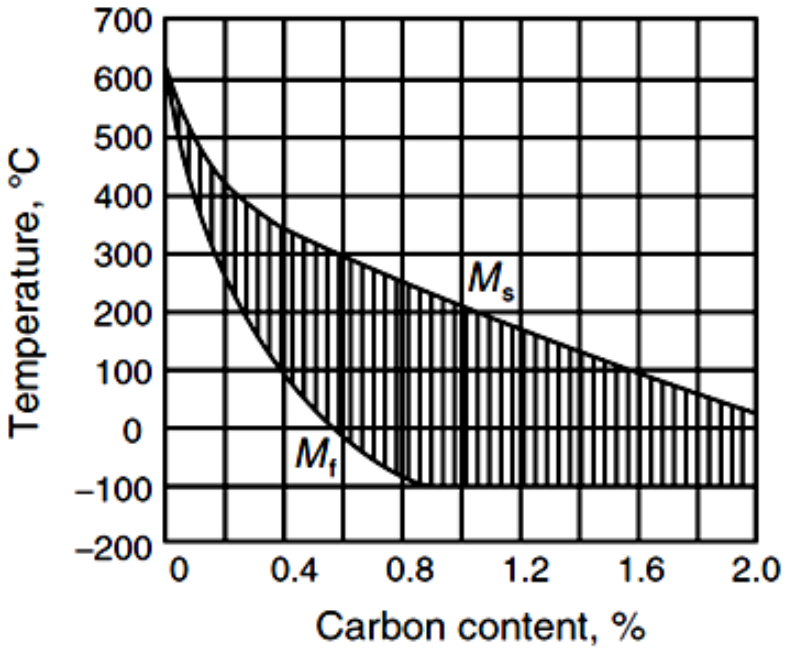



Figure 1.59: Effects of carbon content on the $M_s$ and $M_f$ temperature on carbon steel.

As can be seen from this diagram, when steels of more than 0.65% C are quenched the austenite to martensite transformation does not end at room temperature 20°C but at some lower temperature, even at temperatures much lower than 8°C. Consequently, after these steels are

quenched to room temperature, a portion of austenite (white portion) will remain untransformed; this is referred to as retained austenite, Fig.1.60.

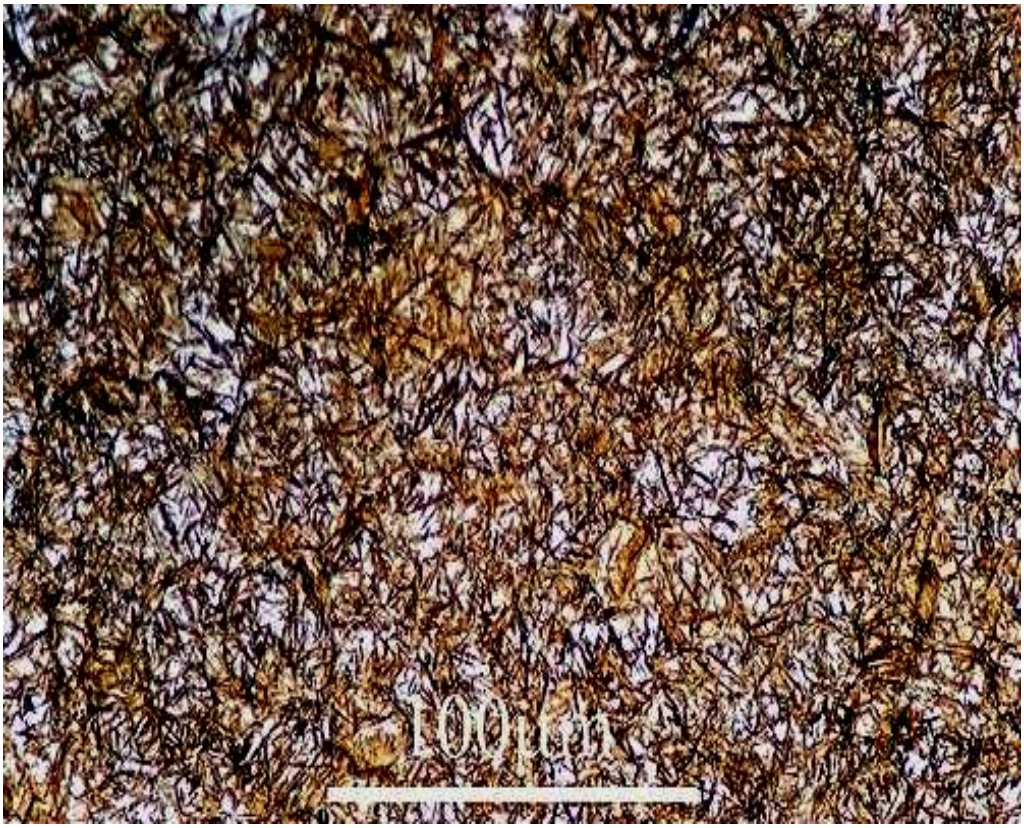


Figure 1.60: Retained austenite along with martensite in quenched carbon steel.

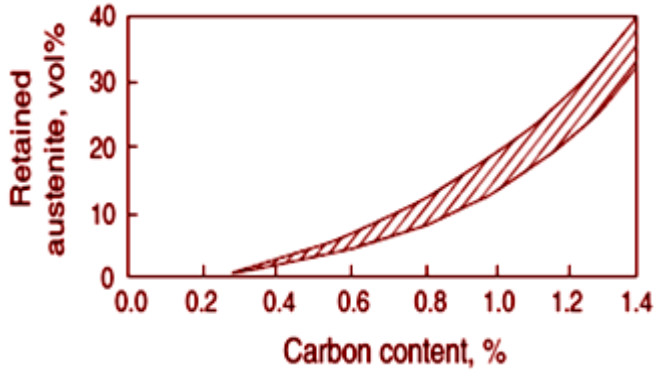



Figure 1.61: Effect of carbon content on the retained austenite content in the as quenched carbon steel.

The greater the amount of carbon in the steel, the greater the amount of retained austenite after quenching. Retained austenite, which is a softer constituent of the structure, decreases the steel's hardness after quenching. If present in amounts of more than 10%, a substantial decrease in the

hardness of the quenched steel may result. Following Fig.1.61 shows the relationship between carbon content and retained austenite in quenched steel.

Other alloying elements also have great influence on the retained austenite content as shown in Fig.1.62.

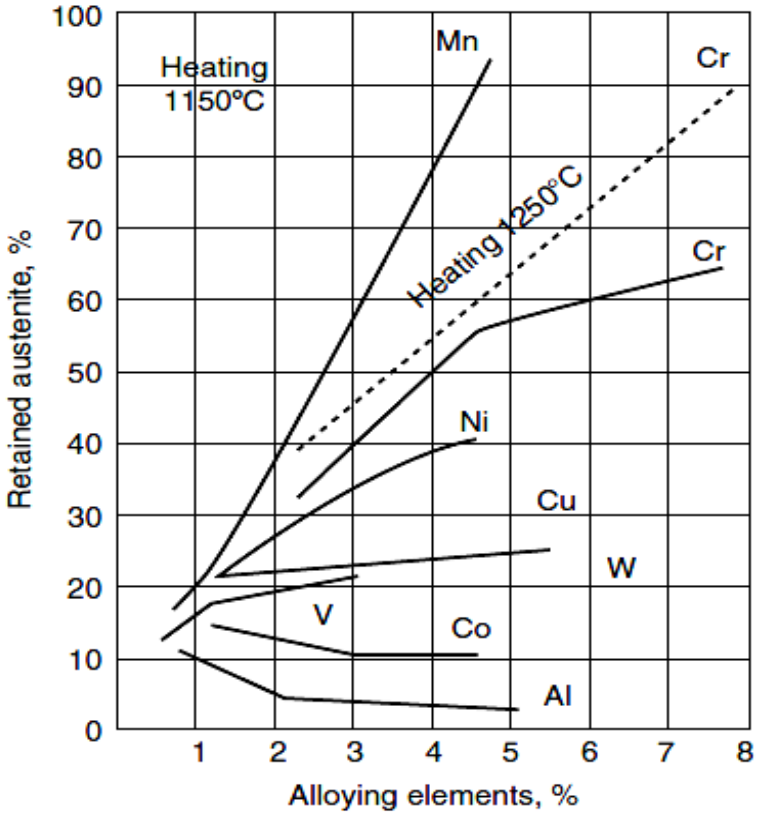



Figure 1.62: Effects of alloying elements on martensite start temperature.

The martensite transformation occurs athermally below $M_s$, i.e., the extent of transformation is proportional to under cooling below the $M_s$ and does not depend on the time spent below the $M_s$. The transformation from austenite to martensite proceeds as the temperature is reduced below $M_s$ until the martensite finish temperature ( $M_f$ ) is reached, at which point 100% martensite is expected. However, if the $M_f$ temperature is below room temperature, then some austenite may be retained if only cooled to room temperature. The martensite transformation is also sensitive to external and internal stresses. Another important feature of martensite transformation in carbon containing steels is that the tetragonal distortion of BCT structure ( a = b≠ c) increases with carbon content, given by the following relation:

$$\frac{c}{a} = 1 + 0.045 \times (\text{wt\% C})$$

An increase in tetragonality also leads to the hardening of martensite. Martensite that forms in low carbon steel (<0.5 wt% C) shows mainly dislocations, whereas martensite that forms from high carbon steels shows twins. A typical example of dislocated martensite formed from 0.05 wt% C steel is shown in Fig.1.63. The martensite was attained even with the presence of a low concentration of carbon by rapid quench conditions attained through resistance spot welding. Transmission electron microscopy shows lath martensite with a high dislocation density.

Figure 1.63: Low carbon martensite after severe quenching.

By morphology, martensite can be divided into two basic types: plate and massive martensite. They are different in shape, mutual arrangement of crystals, substructure, and habit plane. Plate (needle) martensite is found most frequently in high carbon steels, Fig.1.64.

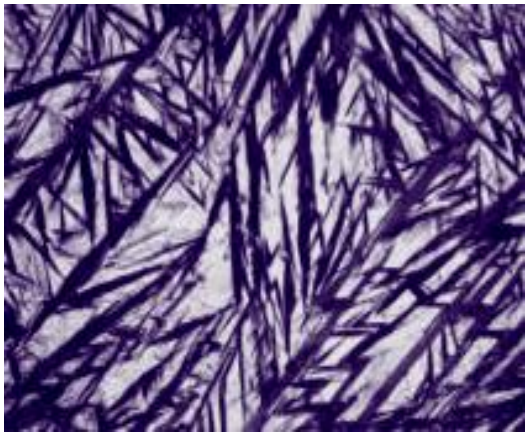


Figure 1.64: Plate or needle like martensite in high carbon steel.

Plates that appear first pass throughout the unit, dividing it into separate parts. But they cannot cross the matrix grain boundary. Therefore, the plate dimension is limited by the dimension of the austenite grain. New martensite plates are formed in austenite sections. If the austenite grain is small, martensite plates are so fine that the needle structure of martensite cannot be seen in it

microsection specimens. Such martensite is called structureless martensite (Fig.1.65) and it is most desirable.

Figure 1.65: Photograph showing the structureless martensite in quenched steel.

Massive (lath) martensite can be observed in low and medium carbon steels. Crystals of this type of martensite are shaped as interconnected plates having approximately the same orientation, Fig.1.66.

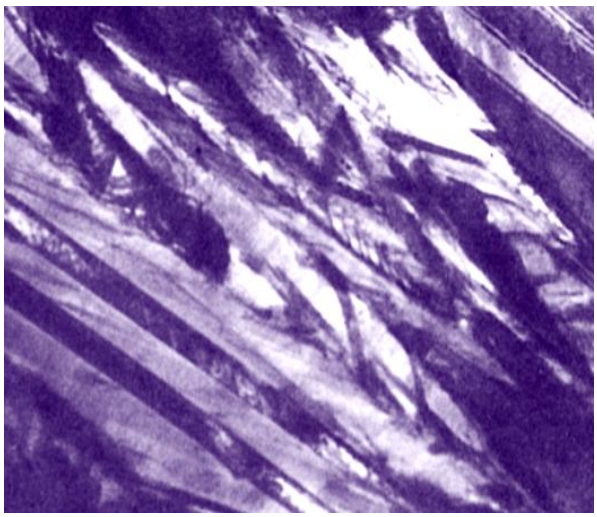


Figure 1.66: Photograph showing the massive lath martensite in quenched steel.

Experiments concerned with the influence of alloying elements on the position of the martensite point show that Co and Al elevate the martensite start temperature, Si has little if any effect, and all the other elements decrease $M_s$, Fig.1.67.

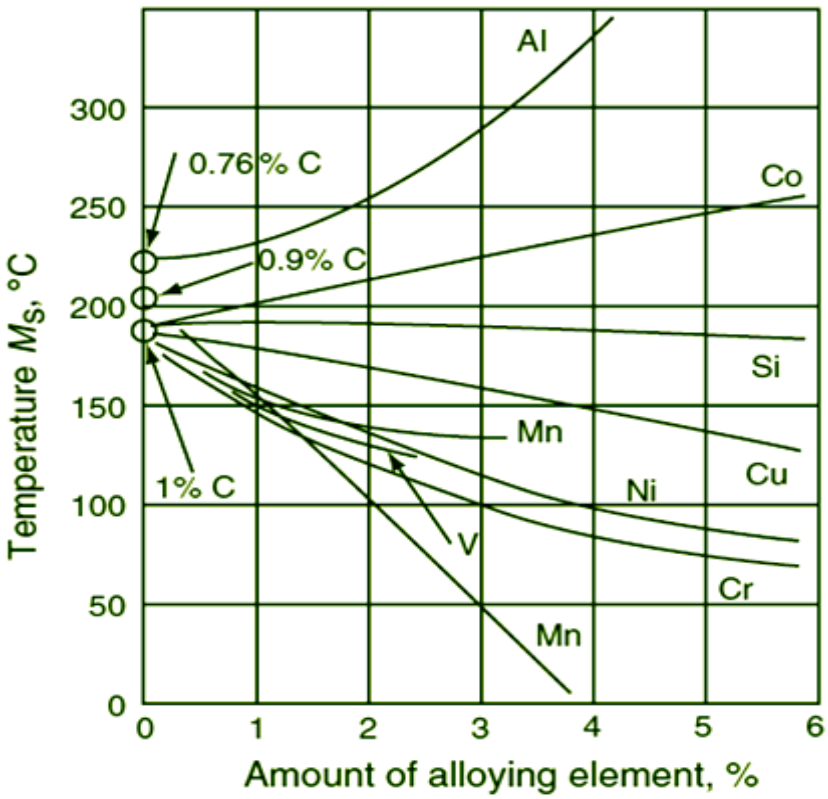



Figure 1.67: Effects of alloying elements on martensite start temperature.

The quantitative influence of alloying elements is approximately as follows (per 1 wt% of the alloying element):

| Element | Mn | Cr | Ni | V | Si | Mo | Cu | Co | Al |
|---|---|---|---|---|---|---|---|---|---|
| Shift of point $M_s$ (°C) | −45 | −35 | −26 | −30 | 0 | −25 | −7 | +12 | +18 (°C) |
| | −81 | −63 | −47 | −54 | 0 | −45 | −13 | +22 | +32 (°C) |

These data are given for carbon steels containing 0.8–1.0% C. For a wider range of C content, the quantitative influence of the elements can be somewhat different. In particular, it was established that the smaller the C content, the weaker is the influence of the alloying elements on the position of point Ms. The martensite start temperature of medium carbon alloy steels can be estimated using empirical formula:

$$M_s\ (^oC) = 520 - 320(\%C) - 50(\%Mn) - 30(\%Cr) - 20(\%Ni + \%Mo + \%V) - 5(\%Cu) + 15(\%Co + \%Al)$$

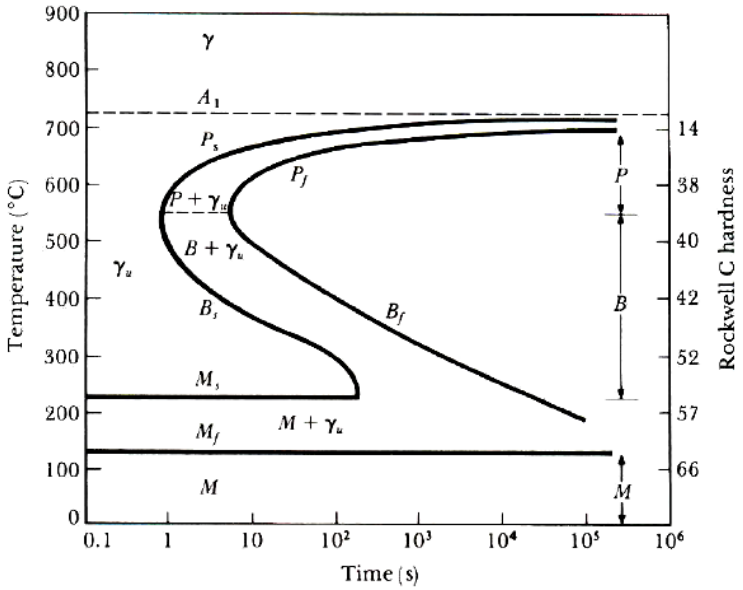
where all elements are in their weight percentages.

The results of calculations by this formula for steels containing 0.2–0.8% C are in good agreement with the experimental data. However, for multi alloy steels this formula does not always yield reliable data because if the steel contains several alloying elements it is impossible to determine their combined effect on the martensite point by simple summation. For example, Mn lowers the point $M_s$ to a greater extent than Ni, but in a steel with a high Cr content its effect is weaker than that of Ni.

The martensite point $M_s$ is affected mostly by C dissolved in austenite. A characteristic feature of the martensite transformation in steels, whatever its character (athermal, explosive, or fully isothermal), is that transformation of austenite to martensite is never complete. The transformation starts at the point $M_s$ and the amount of martensite increases with decrease in temperature rather than having relation with time of cooling. The end of the transformation corresponds to the temperature $M_f$. At this temperature a certain amount of austenite is still left as martensitic transformation never ends.

Investigations show that martensite curves of different steels (both carbon and alloy steels) exhibit approximately the same behaviour. Then, if the martensite finish temperature is below room temperature, the amount of retained austenite should, in a general case, be higher, the lower the martensite point $M_s$. Strictly speaking, the amount of retained austenite depends on the martensite temperature range, i.e., on the $M_s$–$M_f$ temperature difference; it increases as the range narrows. But the martensite range itself depends on the position of the martensite point Ms: the range narrows as the point $M_s$ lowers.

**Problem 1.7**: Excellent combinations of hardness, strength, and toughness are obtained from bainite. One heat treater austenitized a eutectoid steel at 750°C, quenched at a rate of 20°C/s and held the steel at 250°C for 15 min, and finally permitted the steel to cool to room temperature. Did he produce the required bainitic structure? The austenite transformation diagram is below.

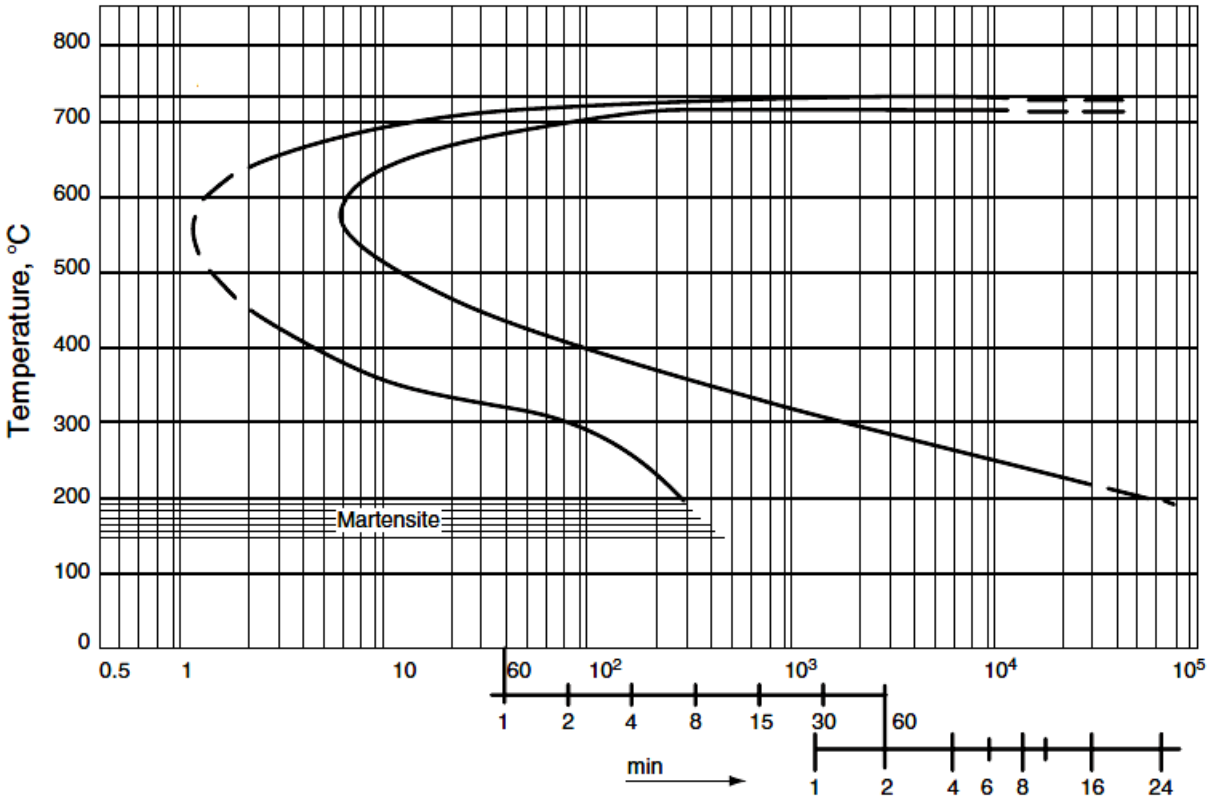


**Solution:** After heating at 750°C, the microstructure is 100% austenite. After quenching to 250°C, unstable austenite remains for slightly more slightly lower than 100s, when fine bainite begins to grow. After 15 min, or 900 s, about 50% fine bainite has formed and the remainder of the steel still contains unstable austenite. As we will see later, the unstable austenite transforms to martensite when the steel is cooled to room temperature and the final structure is a mixture of bainite and hard, brittle martensite. The heat treatment was not successful. The heat treater should have held the steel at 250°C for at least $10^4$s or about 3 h.

**Problem 1.8**: Design a heat treatment schedule to achieve a mixture of bainitic (50% upper bainite and 50% lower bainite) structure using the same transformation diagram.

**Solution**: Self

**Problem 1.9:** AISI 1050 steel is to be hardened isothermally to achieve fully upper bainitic microstructures. Design the heat treatment schedule. The transformation diagram of the the steel is given below.



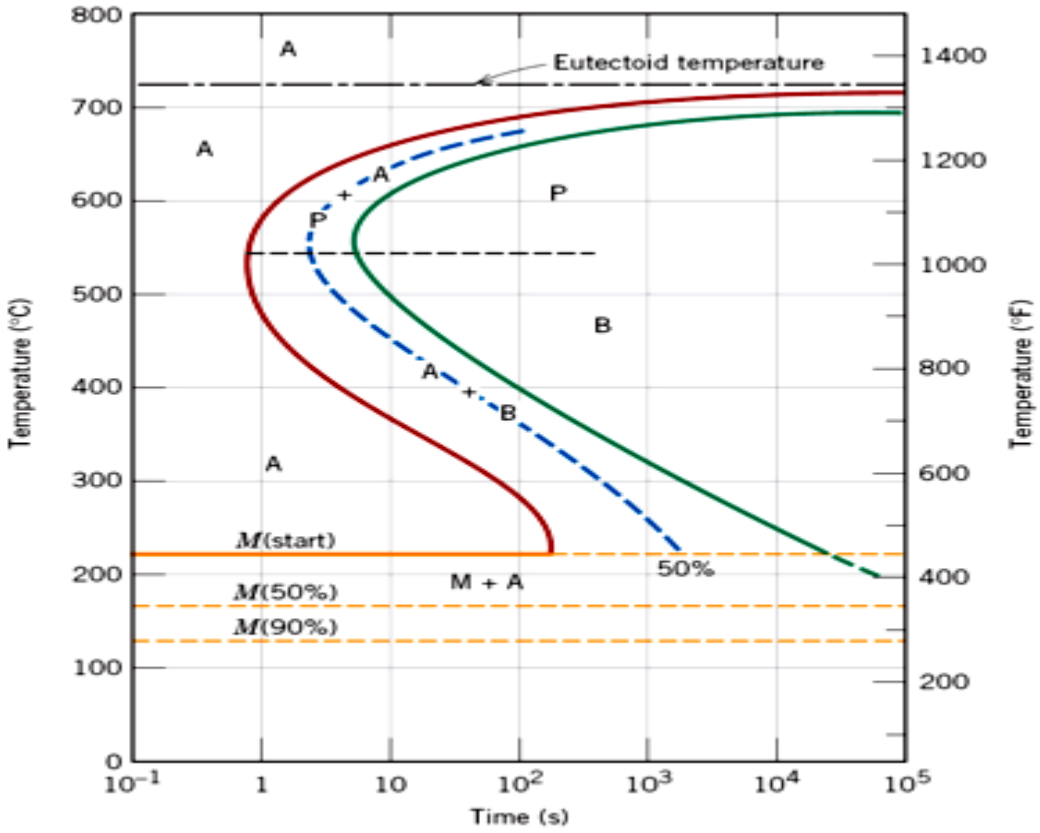

**Problem 1.10:** A typical low alloy steel has the following chemical compositions (in wt%):

| | | | |
|---|---|---|---|
| C = 0.56 | Si = 0.45 | Mn = 0.95 | Cr = 0.50 |
| Ni = 0.6 | S = 0.04 | P = 0.10 | |

Suggest a suitable heat treatment schedule to achieve fully lower bainitic and martensitic structures.

**Solution**: Find out the austenite temperature, $M_S$, $M_f$ and $B_S$ temperatures for the steel. Consider the $M_f$ temperature is 300$^o$C lower than that of the $M_S$ temperature.

**Problem 1.11**: A slightly alloyed 1020 steel cools at 8°C/s when quenched in oil and at 50°C/s when quenched in water. Find the proportions of various phases that might form due to cooling in the mentioned two cooling media. What microstructure is produced by each of the heat treatments? The transformation diagram is given below.




### 1.11.6.4 Tempering of Plain Carbon Steels

The as quenched martensite possesses a complex structure. This occurs in the first formed martensite, i.e. the martensite formed near $M_s$, which has the opportunity of tempering during the remainder of the quench. This phenomenon, which is referred to as auto tempering, is clearly more likely to occur in steels with a high $M_s$. On reheating as quenched martensite, the tempering takes place in four distinct but overlapping stages:

a) Up to 250°C, cause precipitation of ε-iron carbide by subsequent partial loss of tetragonality in martensite

b) Between 200 and 300°C, decomposition of retained austenite to martensite takes place
c) From 250 to 350°C, replacement of ε-iron carbide takes place by cementite
d) Above 350°C martensite loses tetragonality, cementite coarsens and spheroidizes along with recrystallization of ferrite.

It is useful to define a fourth stage of tempering in which the cementite particles undergo a coarsening process and essentially lose their crystallographic morphology, becoming spheroidized. The coarsening commences between 300 and 400°C, while spheroidization takes place increasingly up to 700°C. At the higher end of this range of temperature the martensite lath boundaries are replaced by more equiaxed ferrite grain boundaries by a process which is best described as recrystallization. The final result is an equiaxed array of ferrite grains with coarse spheroidized particles of $Fe_3C$ partly, but not exclusively, in the grain boundaries.

The spheroidization of the $Fe_3C$ rods is encouraged by the resulting decrease in surface energy. The particles, which preferentially grow and spheroidize are located mainly at interlath boundaries and prior austenite boundaries, although some particles remain in the matrix. The boundary sites are preferred because of the greater ease of diffusion in these regions. The original martensite lath boundaries remain stable up to about 600°C, but in the range 350-600°C, there is considerable rearrangement of the dislocations within the laths and at those lath boundaries, which are essentially low angle boundaries. In the as quenched state, martensite, in addition to being very hard, is so brittle that it cannot be used for most applications. Moreover, martensite having high level of residual stress induced during its transformation during quenching have a weakening effect. The ductility and toughness of martensite may be enhanced and these internal stresses relieved by a heat treatment known as tempering. Tempering is accomplished by heating a martensitic steel up to a temperature below the eutectoid for a specified time period.

We know martensite is a supersaturated single phase BCT structure. During tempering it transforms to the tempered martensite, composed of the stable ferrite and cementite phases, as indicated on the iron–iron carbide phase diagram. The microstructure of tempered martensite consists of extremely small and uniformly dispersed cementite particles embedded within ferrite and martensite matrix depending on the tempering temperature. As a result, tempering might reduce very little to a significant decrease in hardness with compatible change in microstructures, Fig.1.68.

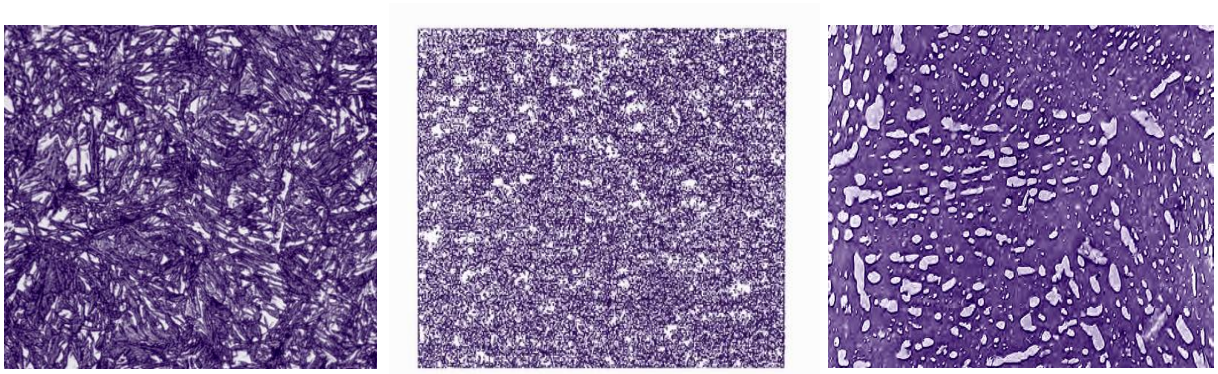


Figure 1.68: Micrographs showing the effect of tempering: Very low temperature tempering (left), moderate temperature tempering (middle) and high temperature tempering (right).

Depending on tempering temperature and time of tempering, formed tempered martensite may be nearly as hard and strong as martensite, but with substantially enhanced ductility and toughness. The effects of tempering temperature on hardness and tensile properties of steel are shown in Figs.1.69 and 1.70.

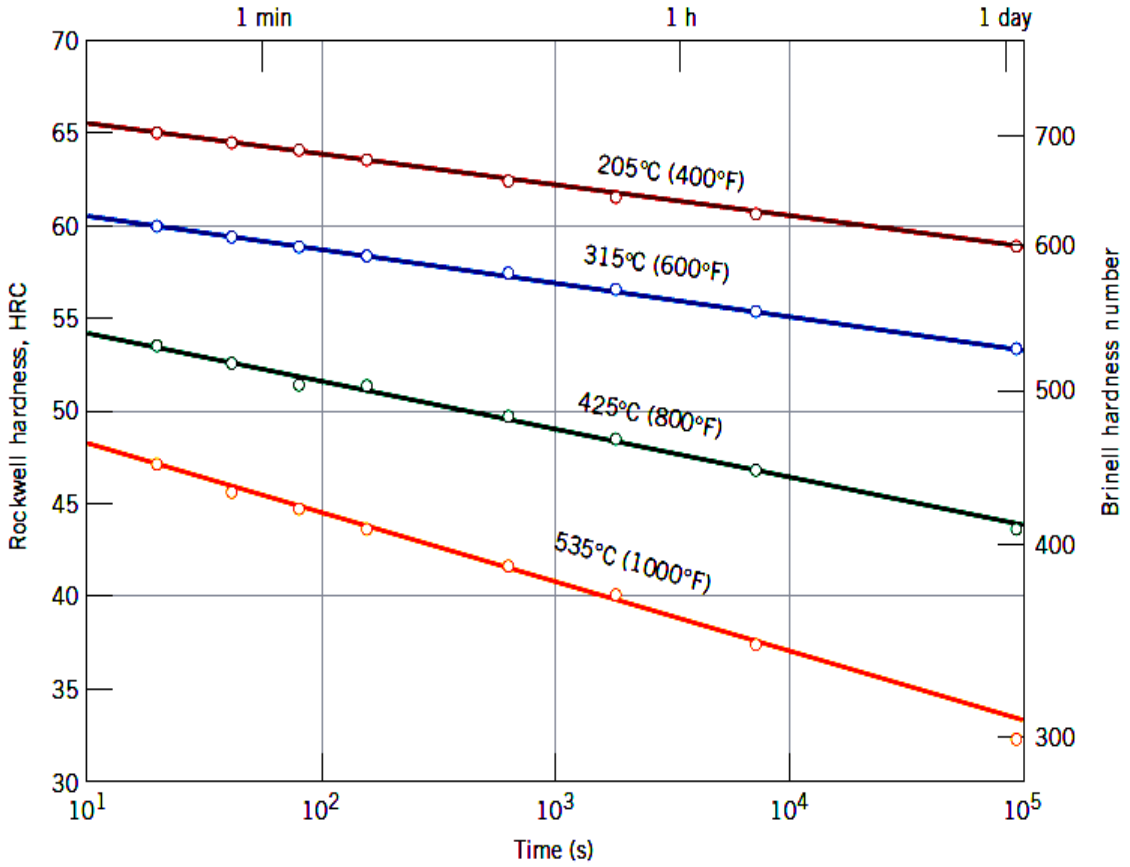



Figure 1.69: Effects of tempering temperatures on hardness values.

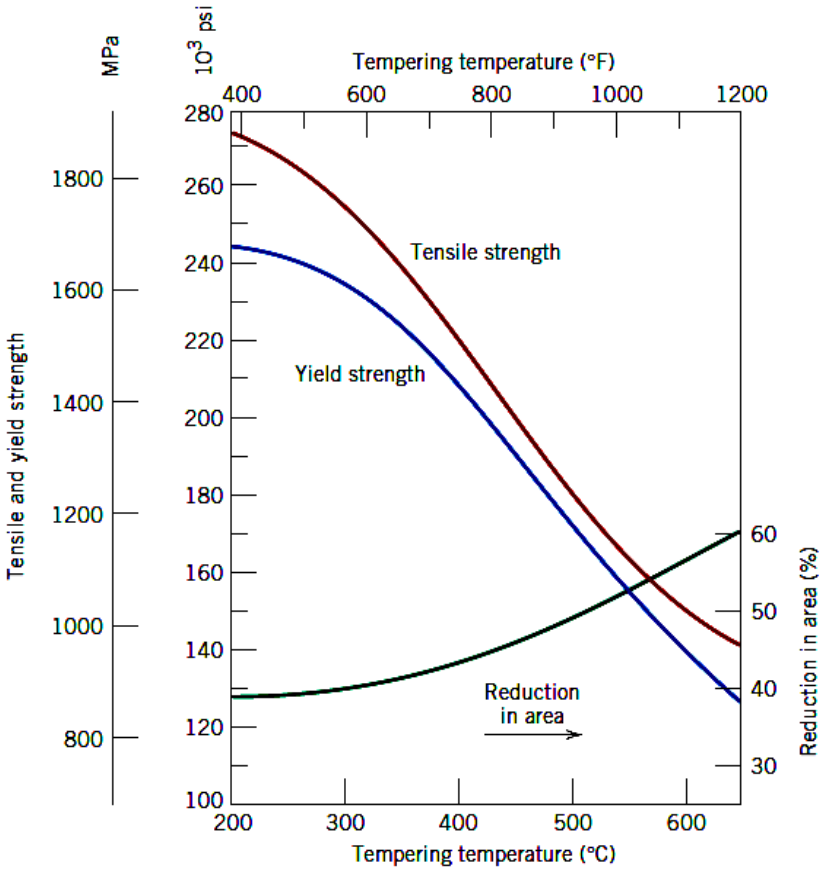



Figure 1.70: Effects of tempering temperature on tensile properties of steel.

### 1.11.6.5 Estimation of Volumetric Change

From time temperature transformation diagram it is clear that there are various microstructures possible on heating and cooling of steel. Furthermore, dimensional changes are possible, depending on the carbon content and microstructural transformation product formed. Following Table summarizes the atomic volumes of different microstructural components as a function of carbon content.

| Phase | Apparent atomic volume, Å$^3$ |
|---|---|
| Ferrite | 11.789 |
| Cementite | 12.769 |
| Ferrite + carbides | 11.786 + 0.163 C(a) |
| Pearlite | 11.916 |
| Austenite | 11.401 + 0.329 C(a) |
| Martensite | 11.789 + 0.370 C(a) |

(a) C = % carbon

Volumetric expansion occurring as a result of quenching can be estimated from the following relationship:

$$(\Delta V/V) \text{ X } 100 = (100 - V_c - V_a) \text{ X } 1.68C + V_a(-4.64 + 2.21C)$$

where $(\Delta V/V)X100$ equals the percentage change in volume, $V_c$ equals the percentage by volume of undissolved cementite, $(100 - V_c - V_a)$ equals the percentage by volume of martensite, $V_a$ equals the percentage by volume of austenite and C equals the percentage by weight of carbon dissolved in austenite and martensite.

If the value of $(\Delta V/V)$ is known or can be computed, then internal stresses that are developed in a part due to temperature differences $(\Delta T)$ arising from either one dimensional heating or cooling can be estimated from:

$$\sigma = E\varepsilon = 1/3(\Delta V/V) = E\alpha\Delta T$$

where $\sigma$ is stress, $\varepsilon$ is strain, *E* (modulus of elasticity) and $\alpha$ is coefficient of thermal expansion $(1.2X10^{-5})$.

**1.11.6.6 Martempering**

Martempering is a term used to describe an interrupted quench from the austenitizing temperature of certain alloy, cast, tool and stainless steels. The purpose is to delay the cooling just above the martensitic transformation for a length of time to equalize the temperature throughout the piece. This will minimize the distortion, cracking and residual stress. The term martempering is somewhat misleading and is better described as marquenching. The microstructure after martempering is essentially primary martensitic that is untempered and brittle. Fig.1.71 given below shows the significant difference between conventional quenching and tempering (left) and martempering (right). Martempering of steel (and of cast iron) consists of:

1) Quenching from the austenitizing temperature into a hot fluid medium (hot oil, molten salt, molten metal, or a fluidized particle bed) at a temperature usually above the martensite range ($M_s$ point).
2) Holding in the quenching medium until the temperature throughout the steel is substantially uniform.
3) Cooling (usually in air) at a moderate rate to prevent large differences in temperature between the outside and the center of the section.
4) Formation of martensite occurs fairly uniformly throughout the workpiece during cooling to room temperature, thereby avoiding formation of excessive amounts of residual stress.

Straightening or forming is also easily accomplished upon removal from the marquenching bath while the part is still hot. The piece will hold its shape upon subsequent cooling in fixturing or in air cooling after removal from the forming die. The marquenching can be accomplished in a variety of baths including hot oil, molten salt, molten metal, or a fluidized particle bed. Martempered parts are tempered in the same manner as conventional quenched parts. The time lapse before tempering is not as critical because the stress is greatly reduced.

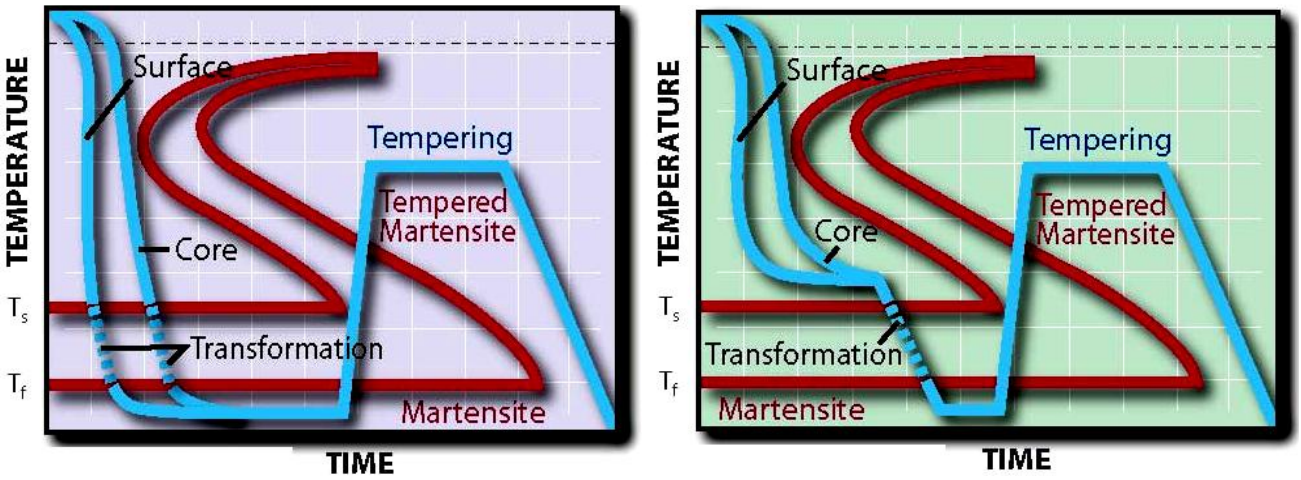



Figure 1.71: Schematic diagrams showing the quenching and tempering (left) and martempering cycle.

### 1.11.6.7 Advantages of Martempering

The advantage of martempering lies in the reduced thermal gradient between surface and center as the part is quenched to the isothermal temperature and then is air cooled to room temperature. Residual stresses developed during martempering are lower than those developed during conventional quenching because the greatest thermal variations occur while the steel is in the relatively plastic austenitic condition and because final transformation and thermal changes occur throughout the part at approximately the same time. Martempering also reduces or eliminates susceptibility to cracking. Another advantage of martempering in molten salt is the control of surface carburizing or decarburizing. When the austenitizing bath is neutral salt and is controlled by the addition of methane gas or proprietary rectifiers to maintain its neutrality, parts are protected with a residual coating of neutral salt until immersed in the marquench bath. Although martempering is used primarily to minimize distortion, eliminate cracking, and minimize residual stresses, it also greatly reduces the problems of pollution and fire hazard as long as nitrate-nitrite salts are used rather than martempering oils. This is especially true where nitrate-nitrite salts are recovered from wash waters with systems that provide essentially no discharge of salts into drains. Any steel part or grade of steel responding to oil quenching can be martempered to provide similar physical properties. The quenching severity of molten salt is greatly enhanced by agitation and water additions to the nitrate salt bath. Both techniques are particularly beneficial in heat treating of carbon steels that have limited hardenability.

### 1.11.6.4 Austempering

Quenchi8g from a temperature above the transformation range to a temperature above the upper limit of martensite formation, and holding at this temperature until the austenite is completely transformed to the desired intermediate structure (Fig.72), for the purpose of conferring certain mechanical properties. Austempering is a hardening process that is used on metals to promote better mechanical properties.

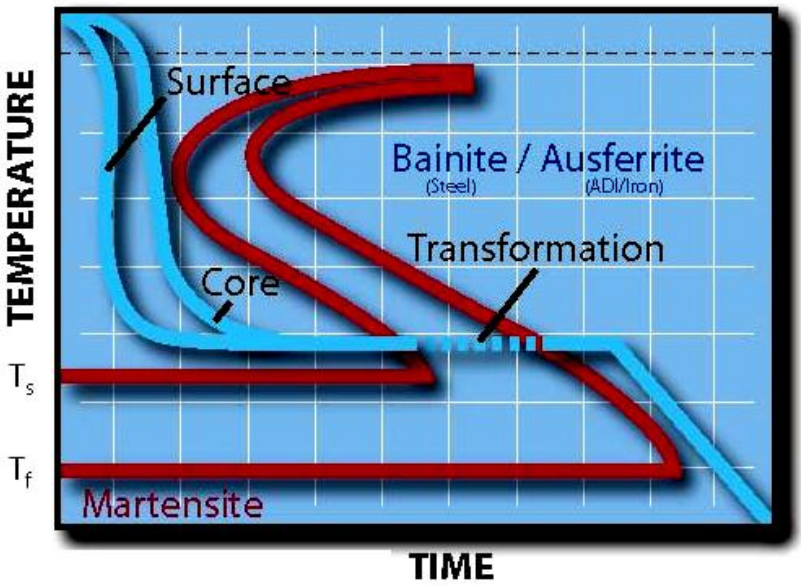



Figure 1.72: Schematic diagram showing the Austempering cycles.

For austempering, he metal is heated into the austenite region and then immediately quenched in a "salt bath" or heat extraction medium that is between temperatures of 300-380$^{o}$C. The metal is held here until the austenite turns to bainite or ausferrite. The part is then removed from the salt bath and rinsed in a room temperature brine to remove excess salts. Since this reaction takes place over several minutes or hours, Austempering produces a material that has uniform growth and a stronger microstructure. Other heat treatments start the same but quench in a medium that is closer to room temperature causing martensite to form. Martensite is a much harder but also more brittle material than bainite. However, a mixture of bainite and martensite of varying proportions (microstructures in Fig.1.73) are possible to maintain by controlling the socking time during austempering, Fig.1.74.

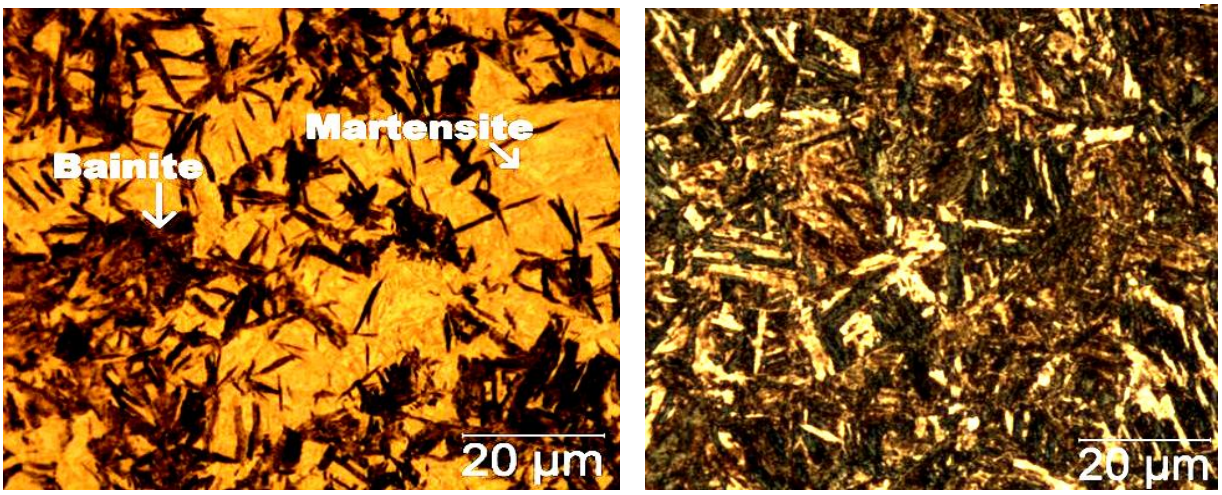



Figure 1.73: Micrographs showing the bainite in martensite (left) and fully bainitic structures (right).

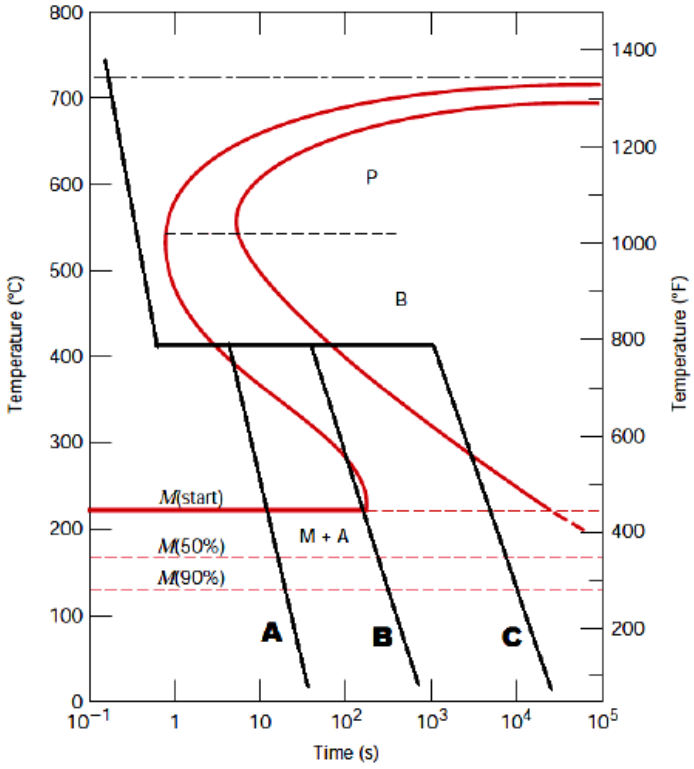



Figure 1.74: Diagram showing the austempering cycles for getting microstructures of various combinations of martensite and bainite.

For getting appropriate amount of bainite and martensite in the austempering heat treatment knowledge on exact bainite transformation start temperature ($B_S$) is very important. The value of $B_S$ depends on the chemical compositions of the steel, which is possible to calculate from the following relationship:

$$B_S\ (°C) = 630 - 45\ Mn\% - 40\ V\% - 35\ Si\% - 30\ Cr\% - 25\ Mo\% - 20\ Ni\% - 15\ W\%$$

The advantages of austempering are listed below.

a) Less distortion
b) Greater ductility
c) Parts are plater friendly due to the clean surface from the salt quench
d) Uniform and consistent hardness
e) Tougher and more wear resistant
f) Higher impact and fatigue strengths
g) Resistance to Hydrogen Embrittlement

Austempering should be used for:

a) Material used: SAE 1045 to 1095, 4130, 4140, 5060, 5160, 6150, 8740, C1050
b) If the material thickness is between 0.008 and 0.150 inches
c) Required hardness needed in between HRC 38-52
d) Material prone to distortion

### 1.12 Quenching Media

When a part is heated to a specified temperature, heat is transferred to it by the furnace. Conversely, when the part is quenched, heat is transferred from it to the surrounding medium. This produces localized temperature gradients where there is conductive heat transfer from the higher temperature region to the lower temperature region. The heat transfer rate per unit area is proportional to the local temperature gradient and can be expressed by Fourier's law of heat transfer:

$$Q = -\lambda A \frac{\delta T}{\delta x}$$

where Q is the heat transfer rate in J/s, λ is the thermal conductivity in J/(smK), A is the unit area in $m^2$, T is the temperature in K, and x is a local coordinate. The minus sign is inserted because the heat flows from higher to lower temperature areas according to the second law of thermodynamics.

The heat capacity $\rho C_p$ of steel does not vary considerably with the chemical compositions. However, the thermal conductivity λ of iron alloys does vary with temperature as illustrated in Fig.1.75 given below.

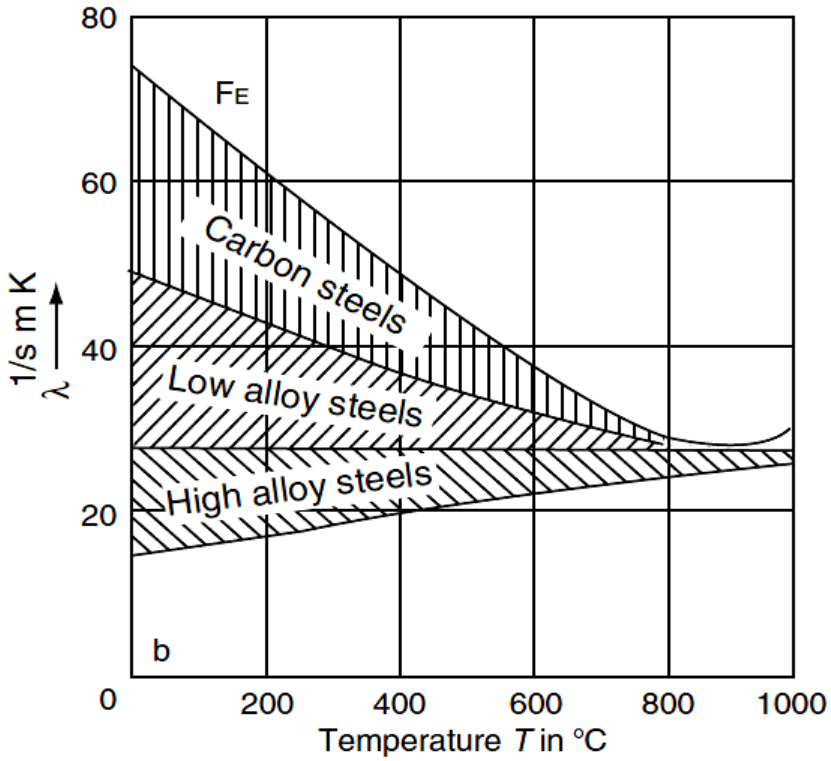


Figure 1.75: Effect temperature on thermal conductivity of the steel component.

At room temperature, the value of λ is drastically reduced with increasing carbon content and to a lesser extent with the content of other alloying elements. The decrease of λ is caused by the distortion of the iron lattice due to insertion of foreign atoms. The thermal conductivities of pure iron, plain carbon steel with 0.45% carbon (1045 steel), and an austenitized (CrNi) stainless steel are 75, 55, and 14-15 W/(mK), respectively. Above 800°C, there is no significant influence of chemical composition on thermal conductivity.

In addition to temperature and alloying elements, thermal conductivity is also influenced by internal stresses and structural changes. Every phase transformation is also accompanied by a change of latent heat and specific volume. Because exact information about the influence of temperature, chemical compositions, structural changes and stresses on the thermodynamic data is not available. Thermal conductivities (J/(smK) of some metals and alloys are given below:

| | |
|---|---|
| Aluminum | 235 |
| Brass | 109 |
| Copper | 401 |
| Gold | 314 |
| Iron | 67 |
| Lead | 35 |
| Nickel | 91 |
| Silver | 428 |

| | |
|---|---|
| Sodium (liquid) | 86 |
| Sodium (solid) | 135 |
| Stainless steel | 14 |
| Steel, Carbon 1% | 43 |
| Thorium (metalic) | 38 |
| Uranium (metalic) | 27.6 |
| Zirconium | 22.6 |
| Zirconium alloy (1% Nb) | 18 |

Another important problem for the determination of the cooling behaviour of steels concerns the heat transfer across the surface of the body to the surrounding medium. This is mathematically described in terms of the (interfacial) heat transfer coefficient α:

$$\alpha = \frac{Q}{A(T_1 - T_2)}$$

where the units of α are J/(sm$^2$K), $T_1$ is the surface temperature of the body, and $T_2$ is the temperature of the medium.

During quenching, the heat transfer coefficient of steel is strongly dependent on the surface temperature and may varies by more than an order of magnitude between the austenitizing and quenchant bath temperatures due to variations in the interfacial film heat transfer such as film boiling and nucleate boiling. The cooling rates of 0.9% carbon steel in various cooling media of different temperatures are shown in Fig.1.76.

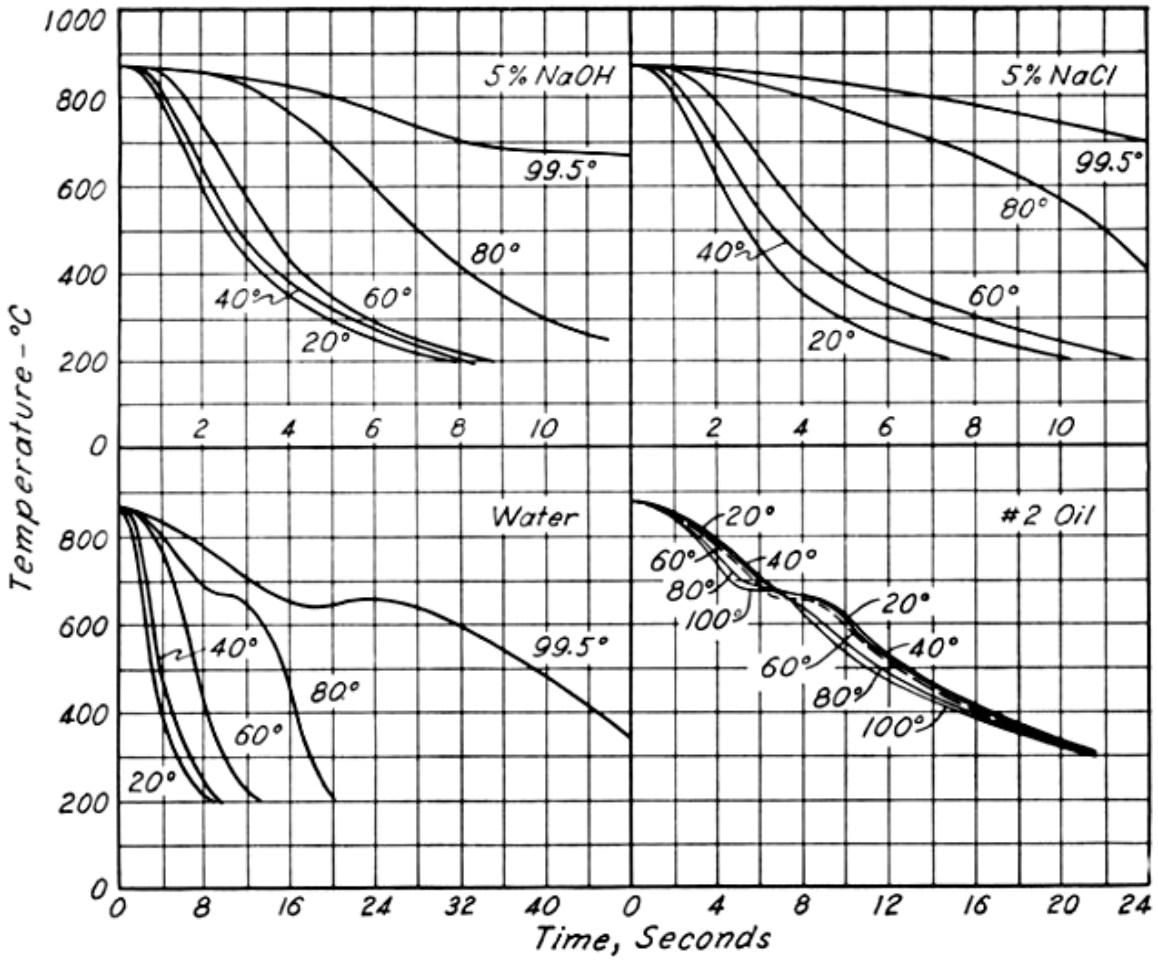



Figure 1.76: Effect of cooling media on cooling rates of 0.9%carbon steel.

From the Fig.1.76 the general observations are:

1. Cooling is rate, in any quenching medium, decreases with increase in the temperature of the medium.
2. Highest cooling rate is resulted in brine, second highest is in NaOH solution, after that the position is for water, whereas, oil results the lowest cooling rate.

### 1.12.1 Various Stages of Cooling in Quenching

Traditionally we talk about three distinct stages of cooling (Fig.1.77). Stage A is called the "vapour blanket" (or "film boiling") stage. It is stage where formation of an unbroken vapour blanket takes place that surrounds and insulates the work piece. It forms when the supply of heat from the surface of the part exceeds the amount of heat that can be carried away by the cooling medium. The stability of the vapour layer is dependent on the metal's surface irregularities, oxides present, surface-wetting additives, etc, which accelerate the wetting process and destabilize the vapour blanket. In this stage, the cooling rate is relatively slow in that the vapour envelope acts as an insulator and cooling is a function of conduction through the vapour envelope.

Stage B is the second stage of cooling known as the "vapour transport" (or "nucleate boiling" or "bubble boiling") stage. It is during this portion of the cooling cycle that the highest heat transfer rates are produced. It begins when the surface temperature of the part has cooled enough so that the vapour envelope formed in Stage A collapses. Violent boiling of the quenching liquid results, and heat is removed from the metal at a very rapid rate, largely due to heat of vaporization. The boiling point of the quenchant determines the conclusion of this stage. Size and shape of the vapour bubbles are important in controlling the duration of this stage. The majority of quenching part distortion occurs during this stage.

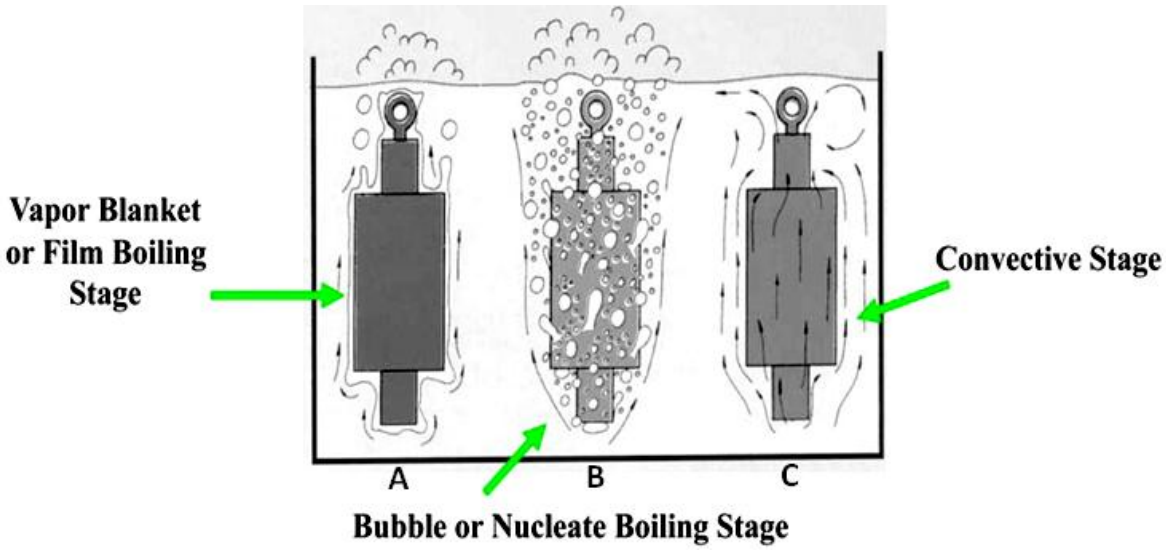



Figure 1.77: Various stages of cooling in quenching.

Stage C is the third stage of cooling called the “liquid” (or “convection”) cooling stage. The cooling rate during this stage is slower than that developed in the second stage and is exponentially dependent on the viscosity of the quenchant. In the case of oil, decomposition takes place initially in a reduction of oil viscosity followed by increasing viscosity as the degradation process increases. Heat transfer rates increase with lower viscosities and decrease with increasing viscosity. This final stage, begins when the temperature of the metal surface is reduced to the boiling point (or boiling range) of the quenching liquid. Below this temperature, boiling stops and slow cooling takes place by conduction and convection. The difference in temperature between the boiling point of the liquid and the bath temperature is a major factor influencing the rate of heat transfer in liquid quenching. Viscosity of the quenchant plays a major role in the cooling rate in this stage. In typical new quenching oil, the cooling rates at different stages are shown in Fig.1.78.

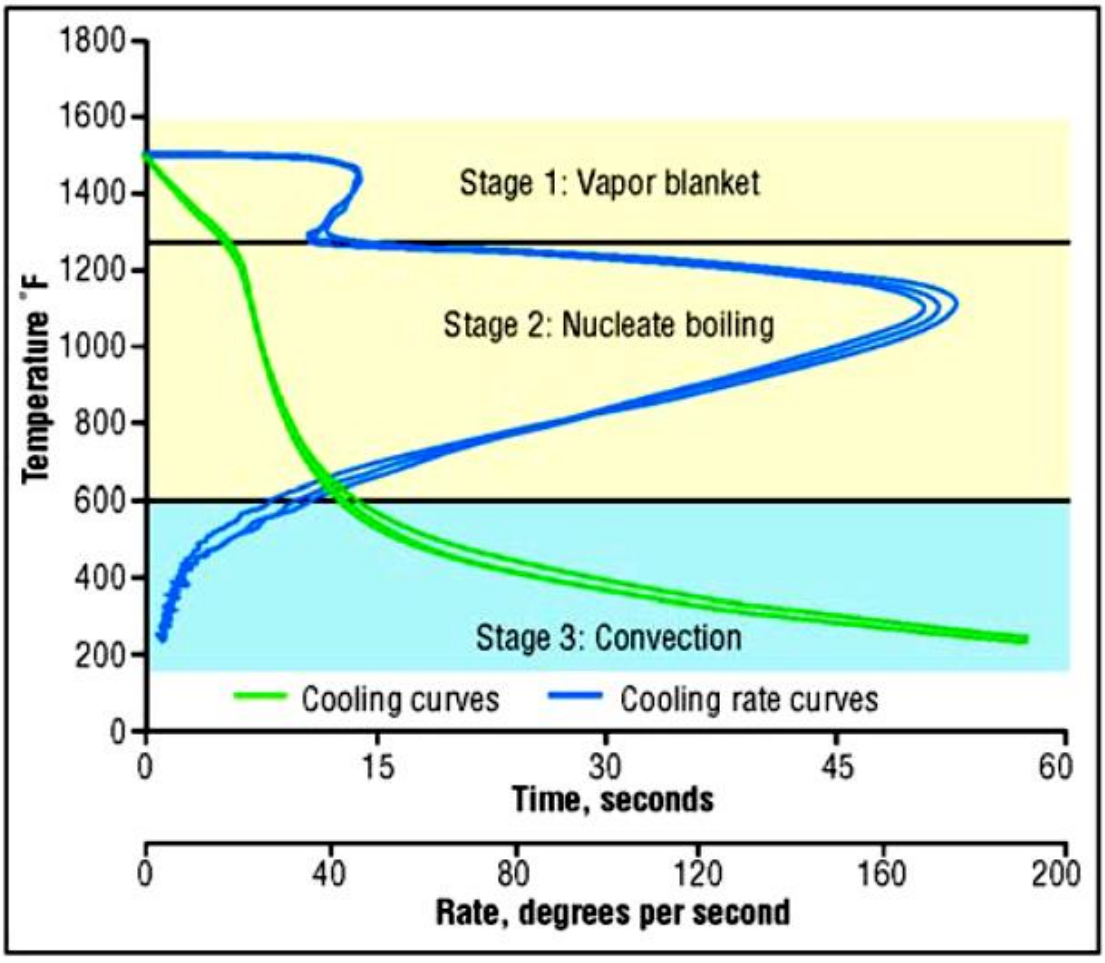



Figure 1.78: Cooling rate in quenching oil at different stages.

In addition, the stages of cooling mentioned above may not occur at all points on a part at the same time, Fig.1.79. As the internal heat moves to the surface differences in heat rejection may vary based on the surface configuration. Consequently, the need for a uniform and controllable

agitation of liquid over the part surface is imperative. Controlled movement of the quenching liquid is vital as it causes an earlier mechanical disruption of the vapour blanket in the first stage and produces smaller, more frequently detached vapour bubbles during the vapour transport cooling stage. Agitation constantly provides a cooler liquid to the part surface providing a greater temperature difference that allows for improved heat rejection.

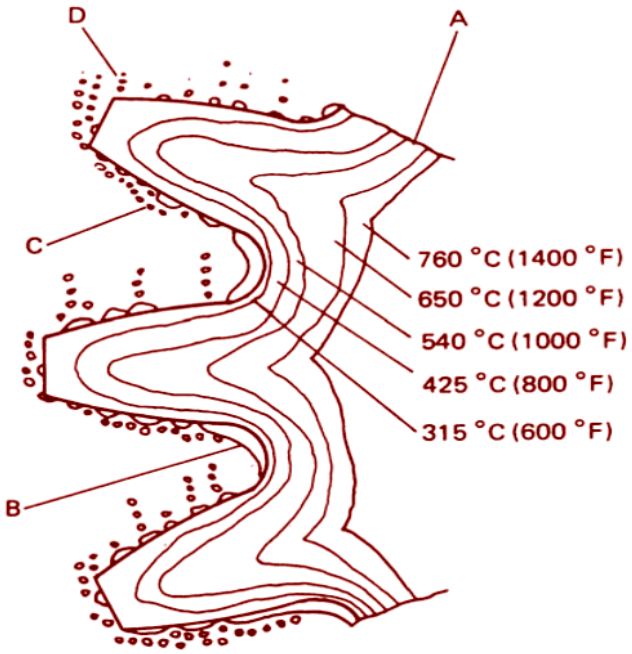



Figure 1.79: Variable cooling rate at different locations of a complex part.

### 1.12.3 Properties of an Ideal Quenching Medium

The ideal quenching medium is one that would exhibit high initial quenching speed in the critical hardening range (through Stage A & B) and a slow final quenching speed through the lower temperature range (Stage C). Thus the ideal quenchant is one that exhibits little or no vapour stage, a rapid nucleated boiling stage and a slow rate during convective cooling. The high initial cooling rates allow for the development of full hardness by getting the steel past the 'nose' of the isothermal transformation diagram (quenching faster than the so-called critical transformation rate) and then cooling at a slower rate beginning at the time the steel is forming martensite. This allows stress equalization; thus, distortion and cracking are reduced. The first criterion that any quenchant must meet is its ability to approach this ideal quenching mechanism.

When conventional quenching oils are used, the duration of Stage A is longer; the cooling rate in Stage B is considerably slower; and the duration of Stage C is shorter. As such, the "quenching power" of oil is far less drastic than that of water. Water and water solutions exhibit high initial cooling rates. Unfortunately, because of water's low boiling point, this fast cooling persists until the steel is cooled to below 300ºF (150ºC). As most steels have formed or are forming martensite by this point, stresses are given little time to equalize. Thus water is typically limited to simple shapes or low hardenability materials. Oil has a major advantage over water due to its higher

boiling range. A typical oil has a boiling range between 450ºF (230ºC) and 900ºF (480ºC). This causes the slower convective cooling stage to start sooner enabling the release of transformation stresses. Oil is, therefore, able to quench intricate shapes and high hardenability alloys successfully. As it is heated, oil has a proportional drop in viscosity. This allows the quenchant to move more freely, increasing, in general, the tendency to break the vapour blanket layer.

The nucleate boiling stage is not drastically altered by changes in bath temperature. The cooling rate in the convection stage of an oil quench will slow as the bath temperature increases. This is advantageous for obtaining a slower rate of cooling through the austenite-to-martensite transformation range. In general, as the temperature of a quenching oil increases, the overall quenching rate increases. Practical heat transfer coefficient (α) values in the 1000 to 2500 $W/m^2K$ range can be achieved depending on oil characteristics and degree of agitation.

## 1.13 Common Treatment Defects

### 1.13.1 Distortion

Due to the heat treatment process, a considerable improvement in physical properties occurs along with some undesirable changes in size & shape. These changes in dimensions occur mainly due to the various stresses (i.e. thermal stresses, stresses developed by the transformation of hardened structure etc.) that are developed by the manufacturing operations. Further, some distortions are also developed during the handling of heat treatment processes at the austenizing temperature, which is more intensified due to rapid heating and cooling, Fig.1.80. In this figure, arrows show direction of stresses. From heating to quenching the part passes various structural changes and internal stress conditions as mention below.

(a) Part heated uniformly throughout. Here, both centre and surface areas are expanded.

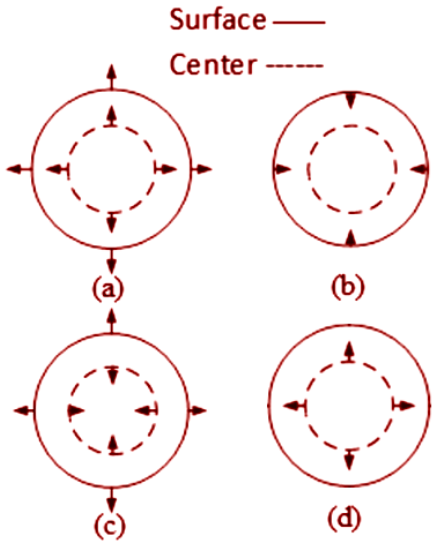



Figure 1.80: Variable cooling rate at different locations of a complex part.

(b) Start of quench, where surface area is contracted more than center.

(c) Midway during quench. Here surface transformed from austenite to martensite. Martensite is relatively less compared to austenite at any fixed temperature. So, surface tries to expand. On the other hand, central portion does not transform to martensite, overall temperature is dropped because of cooling in quenchant. As a result, the central portion tries to contract.

(d) Near end of quench, surface area becomes cold and rigid, center transforming and expanding. Dimensional changes and distortion in the case of case hardened parts are dependent on (1) configuration of the part (2) the process used (3) previous stresses in the part (4) grade of steel used.

Heat treatment is a very tricky job. Deviation from standard practice, lack of facilities, faulty heat treatment equipments, incorrect information concerning the chemical compositions of the components, improper control of heat treatment atmosphere, etc might lead a numerous types of defects in the heat treated components. Some common defects and their remedies are discussed below.

### 1.13.2 Insufficient Hardness

Sometimes the hardness values of the heat treated products might be below to that of the targeted levels. There are various possible reasons regarding the insufficient hardness of the heat treated products some of which are discussed below.

**a) Decarburization**

Decarburization is a process of loss of carbon from the surface of steel or cast iron objects, Fig.1.81. Carbon is the most important alloying element for steel. Decarburaziation decreases the strength, hardness and hardenability of steel component because the saturation level of austenite during heating decreases that subsequently causes lower surface hardness values.

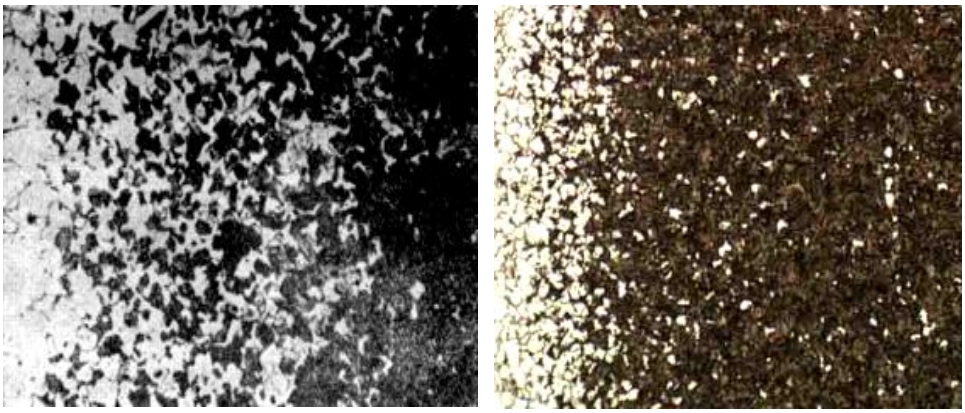


Figure 1.8: Micrographs showing the loss of carbon from carburized steel surface.

In order the avoid decarburization related lower hardness, sufficient machining stock of the stock material for preexisting decarburized surface so that full fresh material is exposed to the surface.

If decarburization is caused during heating and holding period, components should be protected by appropriate anti decarburizing media or heat in a salt bath, protective atmosphere, if possible, heat treatment should be carried out in a vacuum furnace.

**b) Low Hardening Temperature or Too Fast Heating/Uneven Heating**

If the heating temperature is not above upper critical line then some proeutectoid ferrite remains untransformed and on quenching ferrite will remain unchanged causing low hardness zones along with high hardness areas, Fig.1.82. Sometimes, erroneous control instruments may provide wrong temperature. High rate of heating is also another reason of deviation from full austenite transformation/homogenization. So, proper hardening will not be achieved. In this case, all instruments should be checked, where possible, repeat the hardening treatment can be repeated.

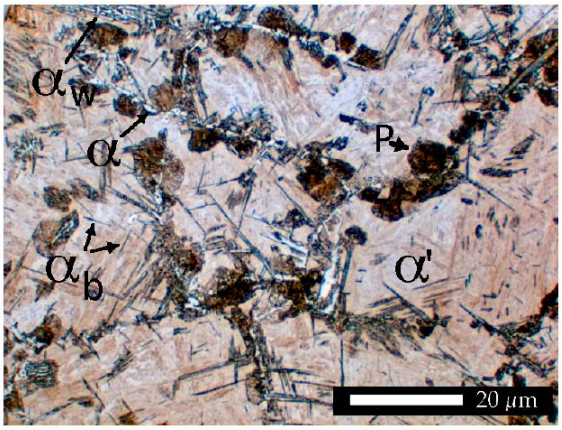



Figure 1.82: Microstructure showing mixed microstructures in quenched steel caused by lack of transformation and homogenization of the austenite.

**c) Insufficient Soaking at Hardening Temperature**

If the holding time is not sufficient, all carbide particles cannot dissolve even the soacking temperature is above the upper critical line. Moreover, insufficient holding time also causes inhomogeneous austenite. On subsequent quenching, it will cause insufficient hardening effect because alloy elements will remain isolated in carbide. So, after quenching, lots of fine and coarse carbides remain in the as quenched martensite, Fig.1.83. The holding times at hardening temperature should always refer to the condition in which the temperature has been reached evenly throughout the entire section. If needed, preheating might be practiced. Where possible, anneal, normalize and repeat the hardening treatment.

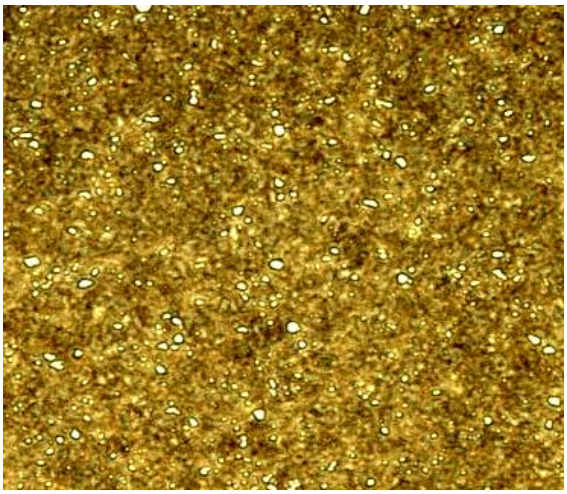


Figure 1.83: Undissolved carbide in the as quenched martensite.

**d) Cooling Rate**

For proper hardening cooling rate is a very important factor. The mechanism of hardening is to get martensitic structures that need critical cooling rate. If the cooling rate is lower than the critical cooling rate (CCR, Fig.1.84) then various low hardness constituents might form, Fig.1.85. Here it is noted that CCR depends on the grade of steel, cooling capacity, sufficient ventilation, surface conditions of the object to be hardened, etc. Such type of problems can be overcome by knowing the chemical compositions of the object and thereby selecting proper cooling media. The volume of cooling media is equally important. In this respect, the relationship between the volume of the cooling medium and the tool must be at least 5:1 with cooling recirculation. In the case of cooling in air, proper ventilation should be mentioned. Clean object should be used for hardening. If there is possibility of oxide formation during heating and holding period, precautions should be taken.

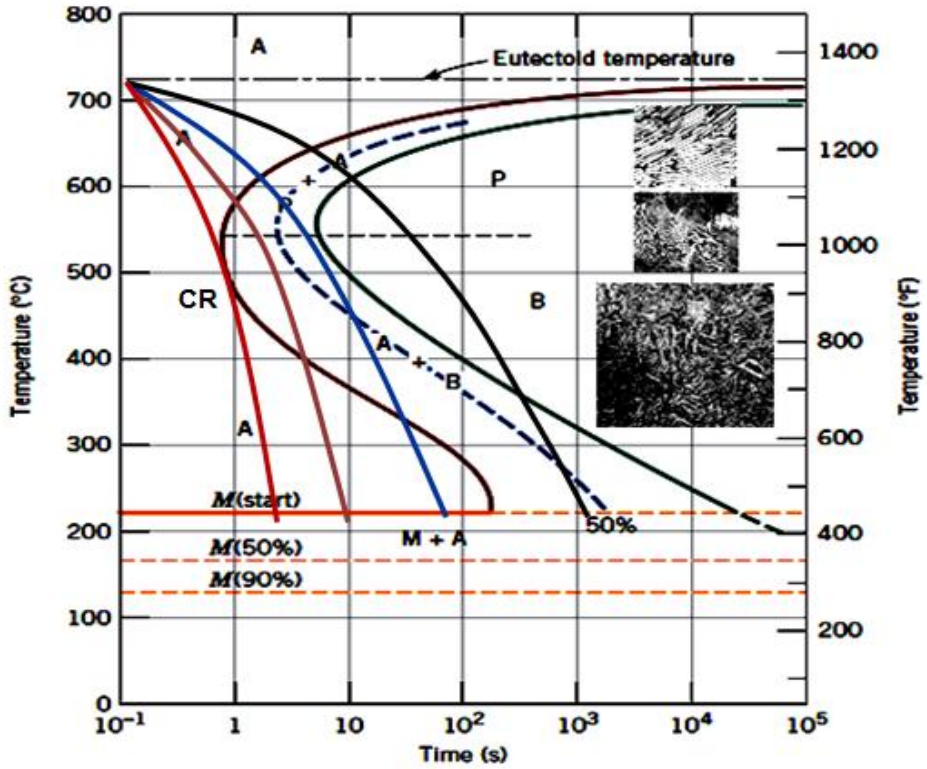



Figure 1.84: Transformation diagram showing the critical cooling rate for martensite formation.

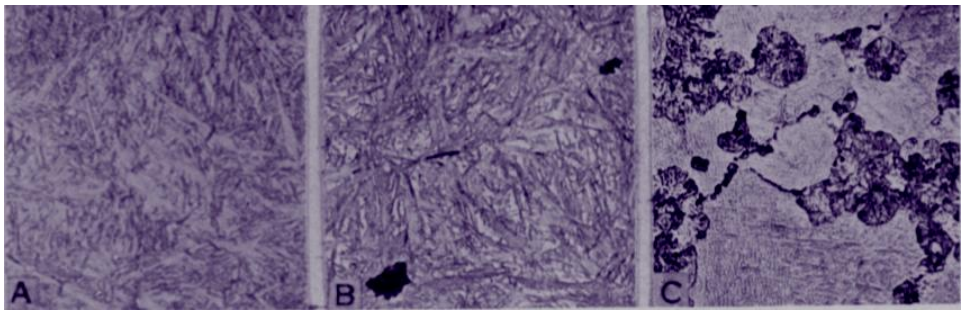



Figure 1.85: Micrographs showing various low hardness constituents in quenched microstructures.

**e) Too High Tempering Temperature**

If the tempering temperature is too high then more carbon will come out from the saturated martensite. So, the residual stress of the martensite fully reduces and tempered martensite is formed. If the tempering temperature is too high then martensitic is transformed to relatively soft fine ferrite and pearlite, Fig.1.86. So, the steel loses its strength significantly. In such cases repetition in hardening followed by tempering at controlled temperature should be done.

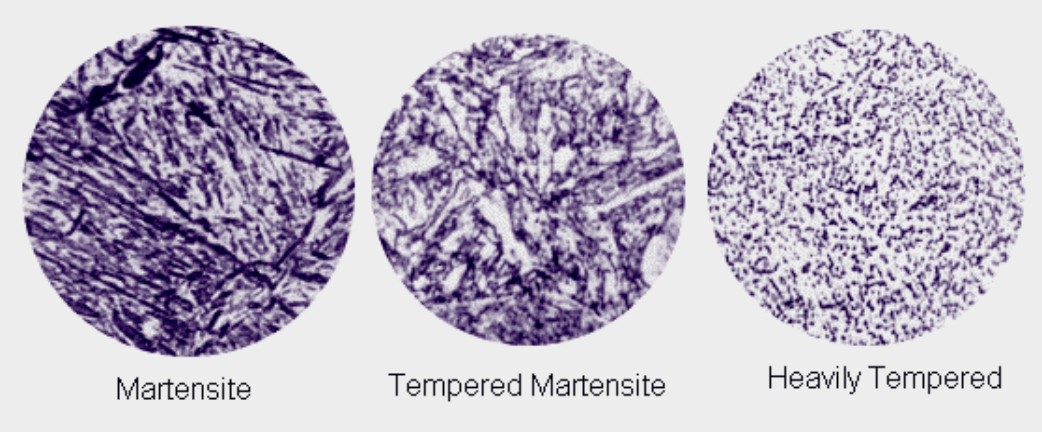



Figure1.86: Effects of high tempering temperature on as quenched martensitic structures.

### 1.13.3 Uneven Hardness

Uneven hardness (Fig.1.87) of the hardened object is usually resulted due to formation of bubbles of steam during cooling, inhomogeneous mixtures used for pack hardening (such as carburizing, chromizing, siliconizing, etc.), decarburization, imperfect surface cleaning, etc. By improper stirring of the quenching bath along with adopting appropriate dipping method, thorough surface cleaning might help to avoid problem related to uneven hardness of the heat treated object.

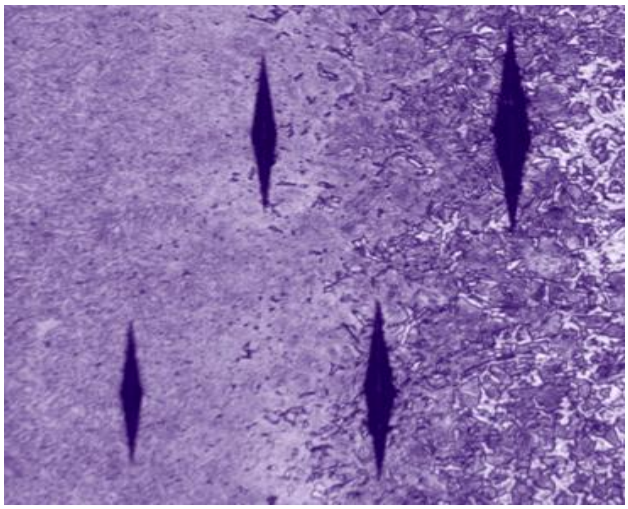


Figure 1.87: Nonuniform hardness on hardened steel component.

### 1.13.4 Excessive Surface Hardness

Surface hardness might be excessively higher than the targeted level, which subsequently causes much residual stress, corrosion attack, vulnerable to impact loading, etc. Moreover, the surface may be cracked. The reasons behind this may be the addition of more carbon from the external source, hardening in improper quenching medium, etc. To avoid this problem proper heating and

quenching media should be used. In the case of salt bath quenching, proportion of salt should be carefully maintained.

### 1.13.5 Deformation

During heat treatment, parts may be deformed because of uneven heating, too fast cooling, parts incorrectly supported in furnace, incorrect dipping in quenching bath, previous stresses present before heat treatment, etc. The overall problems related to deformation may be minimize by preheating the object after rough machining, checking and adjusting furnace parameter, reviewing the methods of supporting and dipping in the quenchant, etc. If the problem still remains, the hardening should be practiced with suitable stress relieving after rough machining. Some examples showing the procedure for dipping of the heated parts to be quenched are shown in Fig.1.88.

Figure 1.88: Quenching process of steel components of various geometries.

In the case of high industrial production rates of similar components automatic systems of heating, quenching, tempering and finishing are utilized, Fig.1.89.

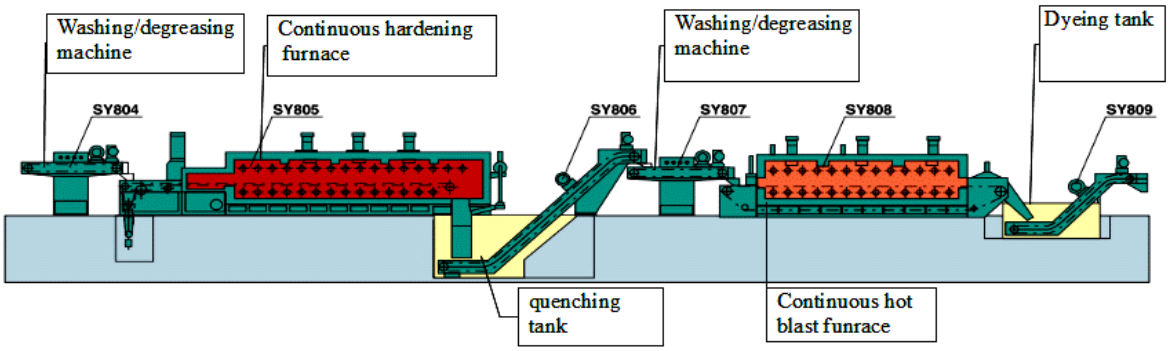



Figure 1.89: Automatic heat treatment system.

### 1.13.6 Cracking and Fracture

There are various reasons for cracking and fracture (Fig.1.90) in the heat treated parts such as uneven heating, too fast cooling, overheating, incomplete transformations that continue with the cooling of tool, retained austenite, insertion of the tools in the furnace without preheating for tempering, etc. These problems related to fracture might be avoided by preheating, selecting the cooling medium according to the shape of the tool and hardenability of the steel, reduce the hardening temperature, tempering immediately after hardening, proper homogenization in soaking period, etc.

Figure 1.90: Fracture in quenched steel components.

Residual stresses and cracking are also developed because of the volume change during heat treatment period and also during cold working. A stress relief anneal can be used to remove or minimize residual stresses due to cold working. Stresses are also induced because of thermal expansion and contraction. In steels, there is one more mechanism that causes stress. When steels are quenched, the surface of the quenched steel cools rapidly and transforms to martensite. When the austenite in the center later transforms, the hard surface is placed in tension, while the center is compressed. If the residual stresses exceed the yield strength, quench cracks form at the surface (Fig.1.91).

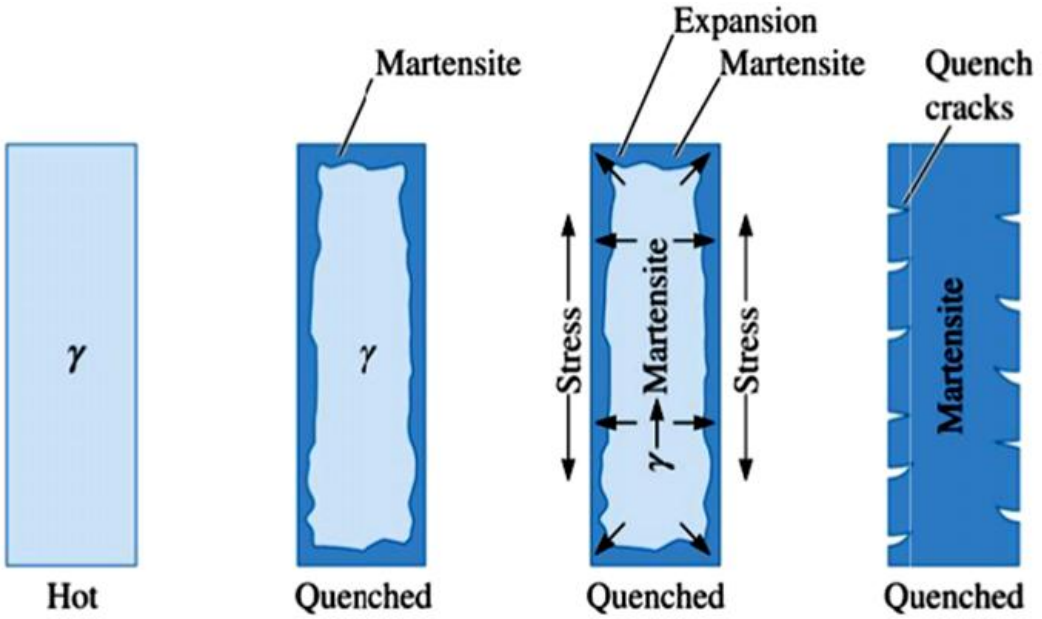



Figure 1.91: Mechanism of crack formation in quenched steel components.

# Chapter Two

# Hardenability of Steel

## 2.1 Definition of Hardenability

Hardenability, in general, is defined as the ability of a ferrous material to acquire hardness after austenitization and quenching. This general definition comprises two sub-definitions: the ability to reach a certain hardness level and the hardness distribution within a cross section. It depends, first of all, on the carbon content of the material and more specifically on the amount of carbon dissolved in the austenite after the austenitizing treatment, because only this amount of carbon takes part in the austenite to martensite transformation and has relevant influence on the hardness of martensite. Figure 2.1 shows the approximate relationship between the hardness of the structure and its carbon content for different percentages of martensite.

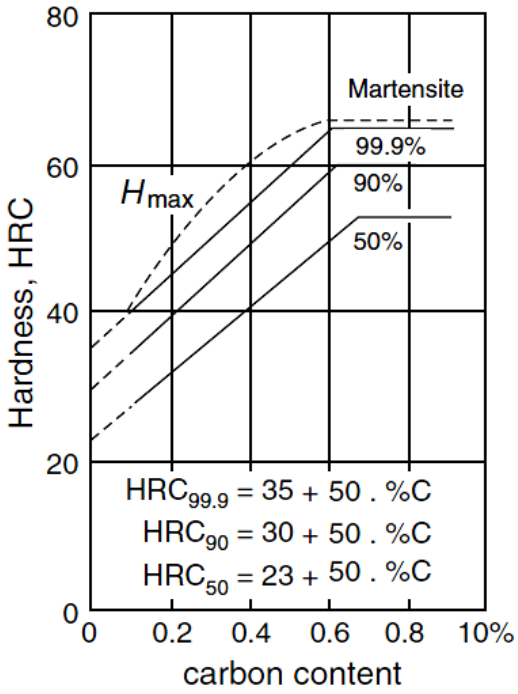
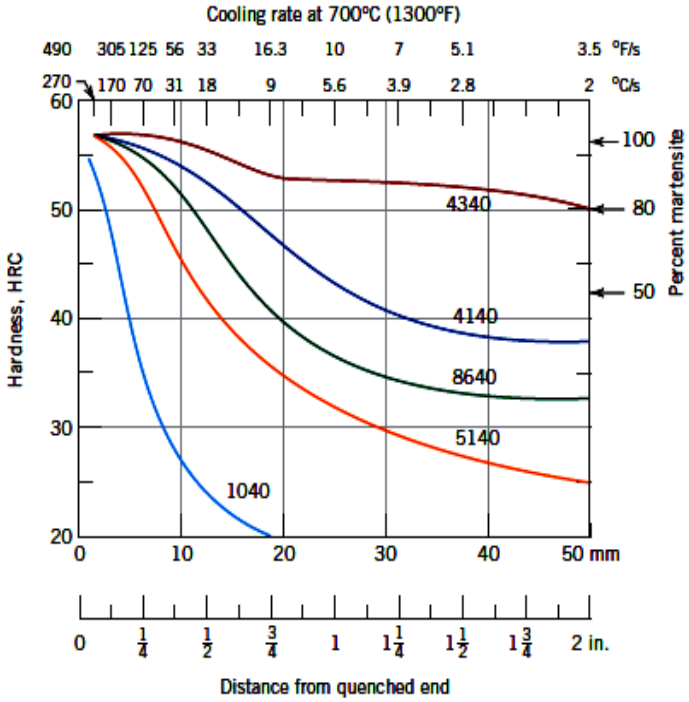



Figure 2.1: Approximate relationship between hardness in HRC and carbon content for different percentages of martensite.

The hardness distribution within a cross section is associated with the change of hardness from the surface of a specified cross section toward the core after quenching under specified conditions. It depends on carbon content and the amount of alloying elements dissolved in the austenite during the austenitizing treatment. It may also be influenced by the austenite grain size. Figure 2.2 shows the hardness distributions within the cross sections of bars of 50mm diameter after quenching five different kinds of steels. In spite of quenching in the same cooling media,

steel 4340 shows the highest hardenability, whereas 1040 showed the lowest level of hardenability. Because, 1040 is plain carbon steel and 4340 contains the highest level of alloying elements.




**1040: 0.4%C**

**5140: 0.4%C, 0.85Cr**

**8640: 0.4%C, 0.55Ni, 0.5Cr, 0.2Mo**

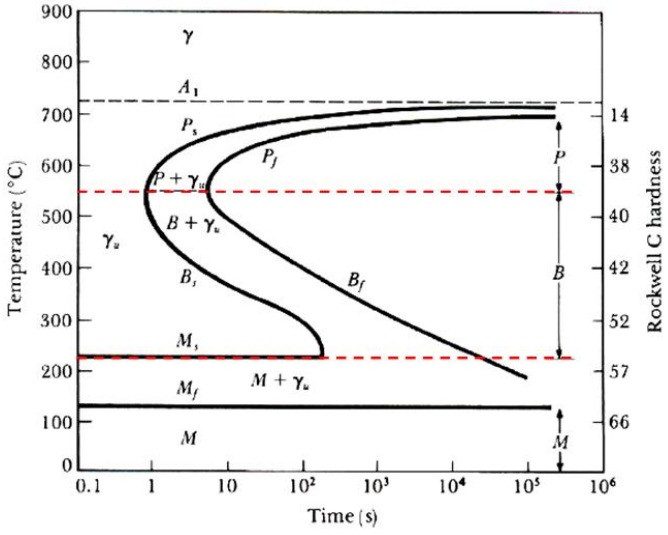
**4140: 0.4%C, 1.0Cr, 0.2Mo**

**4340: 0.4%C, 1.85Ni, 0.8Cr, 0.25%Mo)**

Figure 2.2: Effect of alloying elements on hardenability of steels.

When a steel has high hardenability it achieves a high hardness throughout the entire heavy section (Fig.2.2), even when it is quenched in a milder quenchant (e.g., oil). When a steel has low hardenability its hardness decreases rapidly below the surface, even when it is quenched in severe quenchant (water).

**Problem 2.1:** A steel shaft has 0.8% carbon. After quenching, throughout the whole section, the required hardness is 55. Design the heat treatment schedule. Use Fig.2.1.



## 2.2 Factors Influencing Depth of Hardening

Depth of hardening is usually defined as the distance below the surface at which a certain hardness level (e.g., 50 HRC) has been attained after quenching. Sometimes it is defined as the distance below the surface within which the martensite content has reached a certain minimum percentage. As a consequence of the austenite to martensite transformation, the depth of hardening depends on the following factors:

a) Shape and size of the cross section the workpiece
b) Chemical compositions
c) Quenching media and conditions

Quenching conditions include not only the specific quenchant with its inherent chemical and physical properties, but also important process parameters such as bath temperature, agitation rate and so on. The cross sectional shape has a remarkable influence on heat extraction during quenching and consequently on the resulting hardening depth. Bars of rectangular cross sections always achieve less depth of hardening than round bars of the same cross sectional size because of higher available surface area of heat dissipation during cooling in the quenchant.

## 2.3 Determination of Hardenability

### 2.3.1 Grossmann's Hardenability Concept

Grossmann's method of testing hardenability uses a number of cylindrical steel bars of different diameters hardened in a given quenching medium. After sectioning each bar at mid-length and examining it metallographically, the bar that has 50% martensite at its center is selected and the diameter of this bar is designated as the critical diameter ($D_{crit}$). The hardness value corresponding to 50% martensite will be determined exactly at the center of the bar of $D_{crit}$. Other bars with diameters smaller than $D_{crit}$ have more than 50% martensite in the center of the cross section and correspondingly higher hardness, while bars having diameters larger than $D_{crit}$ attain 50% martensite only up to a certain depth as shown in Fig.2.3. The critical diameter $D_{crit}$ is valid for the quenching medium in which the bars have been quenched. If one varies the quenching medium, a different critical diameter will be obtained for the same steel.

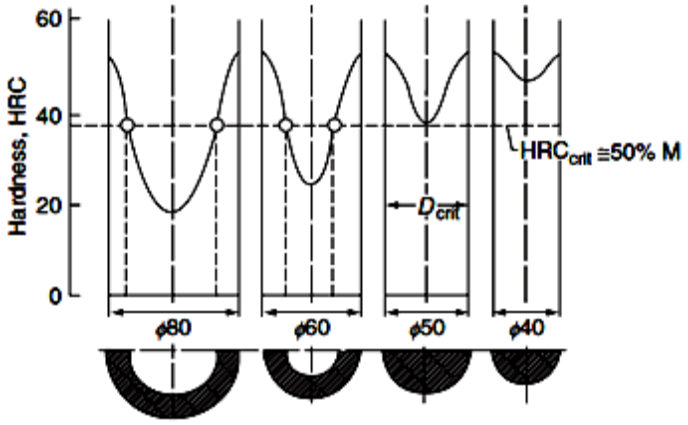



Figure 2.3: Determination of the critical diameter $D_{crit}$ according to Grossmann.

To identify a quenching medium and its condition, Grossmann introduced the quenching intensity (severity) factor H. The H values for oil, water, and brine under various rates of agitation are given in Table 2.1.

Table 2.1: Quenching intensity factors of various cooling media.

| | H Value (in.$^{-1}$) | | |
|---|---|---|---|
| **Method of Quenching** | **Oil** | **Water** | **Brine** |
| No agitation | 0.25–0.30 | 1.0 | 2.0 |
| Mild agitation | 0.30–0.35 | 1.0–1.1 | 2.0–2.2 |
| Moderate agitation | 0.35–0.40 | 1.2–1.3 | |
| Good agitation | 0.40–0.50 | 1.4–1.5 | |
| Strong agitation | 0.50–0.80 | 1.6–2.0 | |
| Violent agitation | 0.80–1.10 | 4.0 | 5.0 |

From this table, the large influence of the agitation rate on the quenching intensity is evident. To determine the hardenability of a steel independently of the quenching medium, Grossmann introduced the ideal critical diameter $D_I$, which is defined as the diameter of a given steel that would produce 50% martensite at the center when quenched in a bath of quenching intensity H = $\propto$. Here, H = $\propto$ indicates a hypothetical quenching intensity that reduces the surface temperature of the heated steel to the bath temperature in zero time. For low and medium alloy steels, hardenability as determined by $D_I$ may be calculated from the chemical compositions after accounting for austenite grain size. First, the basic hardenability of the steel as a function of carbon content and austenite grain size is calculated from Fig.2.4 according to the weight percent of each element present.

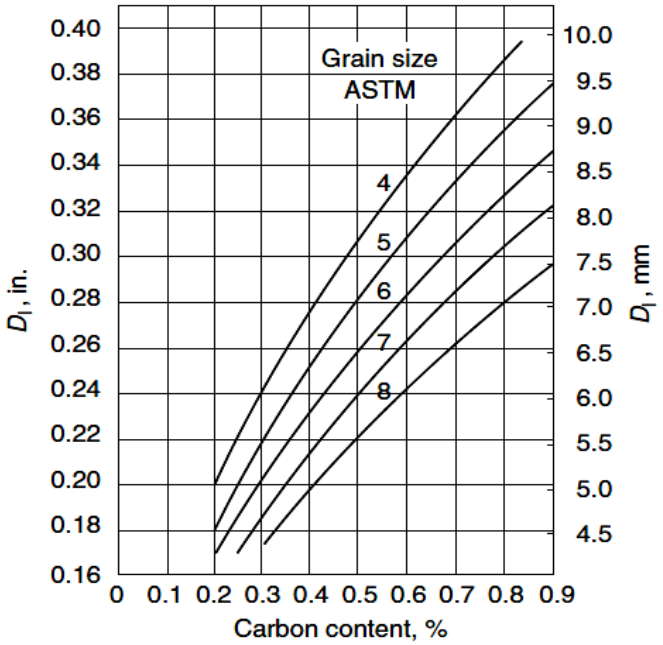



Figure 2.4: The ideal critical diameter (DI) as a function of the carbon content and austenite grain size for plain carbon steels, according to Grossmann.

For example, if a steel has an austenite grain size of American Society for Testing and Materials (ASTM) 7 and the chemical composition C 0.25%, Si 0.3%, Mn 0.7%, Cr 1.1%, Mo 0.2%, then the basic value of hardenability from Fig.4 (in inches) is $D_I = 0.17$. The total hardenability of this steel is:

$$D_I = 0.17 \times 1.2 \times 3.3 \times 3.4 \times 1.6 = 3.7\,\text{in}$$

The multiplying factor of various alloying to be used in calculating the actual hardenability of the alloy can be found from the following diagram, Fig.2.5.

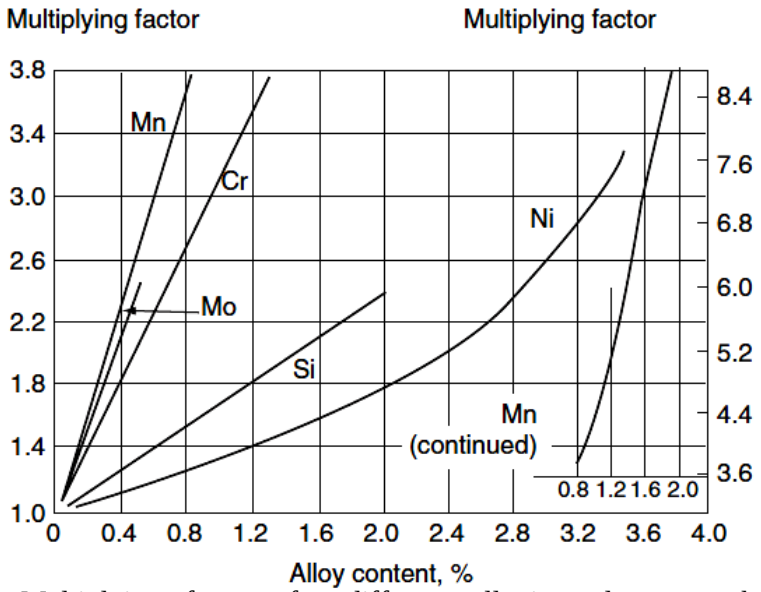



Figure 2.5: Multiplying factors for different alloying elements when calculating hardenability as $D_I$ value, according to AISI.

The ASTM grain size number and corresponding grain diameter is presented in the following Table 2.2.

Table 2.2: ASTM grain sizes.

Average grain diameter for each of the common ASTM grain sizes

| ASTM Grain Size | Grain Diameter (μm) |
|---|---|
| 0 | 359 |
| 1 | 254 |
| 2 | 180 |
| 3 | 127 |
| 4 | 90 |
| 5 | 64 |
| 6 | 45 |
| 7 | 32 |
| 8 | 22.4 |
| 9 | 15.9 |
| 10 | 11.2 |
| 11 | 7.94 |
| 12 | 5.61 |
| 13 | 3.97 |
| 14 | 2.81 |

**Note: Try to practice related issue concerning hardenability.**

### 2.3.2 Hardenability in High Carbon Steels

The hardenability effect of carbon and alloying elements in high-carbon steels and the case regions of carburized steels differ from those in low and medium carbon steels and are influenced significantly by the austenitizing temperature and prior microstructure (normalized or spheroidize annealed). Using Grossmann's method for characterizing hardenability in terms of the ideal critical diameter DI, multiplying factors for the hardenability effects of Mn, Si, Cr, Ni, Mo, and Al were successfully derived for carbon levels ranging from 0.75 to 1.10% C in single-alloy and multiple-alloy steels quenched at different austenitizing temperatures from 800 to 930$^{o}$C. These austenitizing temperatures encompass the hardening temperatures of hypereutectoid tool steels, 1.10% C bearing steels, and the case regions of carburized steels. All of these steels, when quenched, normally contain an excess of undissolved carbides, which means that the quantity of carbon and alloying elements in solution could vary with the prior microstructure and the austenitizing conditions. The hardenability of these steels is influenced by the carbide size, shape, and distribution in the prior microstructure and by austenitizing temperature and time. Compared to this, grain size exhibits a lesser effect.

As a rule, homogenous high carbon alloy steels are usually spheroidize annealed for machining prior to hardening. Carburizing steel grades are either normalized, i.e., air cooled, or quenched in oil directly from the carburizing temperature before reheating for hardening. So different case microstructures (from martensite to lamellar pearlite) may be present, all of which transform to austenite rather easily during reheating for hardening. During quenching, however, the undissolved carbides will nucleate pearlite prematurely and act to reduce hardenability. In spheroidize annealed steels, the carbides are present as large spheroids, which are much more difficult to dissolve when the steel is heated for hardening. Therefore, the amount of alloy and carbon dissolved is less when one starts with a spheroidized rather than a normalized or quenched microstructure. Nevertheless, it has been demonstrated that a spheroidized prior microstructure actually yields higher hardenability than a prior normalized microstructure, at least for austenitizing temperatures up to approximately 855$^{o}$C. This effect occurs because larger carbides are not as efficient nuclei for early pearlite formation upon cooling as fine and lamellar carbides and the nuclei are present in lower numbers. With either prior microstructure, if strict control is maintained over austenitizing temperature and time, the solution of carbon and alloy can be reproduced with sufficient consistency to permit the derivation of multiplying factors. For all calculations, it was important to establish whether pearlite or bainite would limit hardenability because the effects of some elements on these reactions and on hardenability differ widely.

Excellent agreement was obtained between the case hardenability results of carburized steels assessed at 1.0% carbon level and the basic hardenability of the 1.0% C steels when quenched from the normalized prior structure. It was thus confirmed that all multiplying factors obtained

with prior normalized 1.0% C steels could be used to calculate the hardenability of all carburizing grades that are reheated for hardening following carburizing. Jatczak and Girardi determined the difference in multiplying factors for prior normalized and prior spheroidize annealed structures as shown in Figs.2.4 and 2.5.

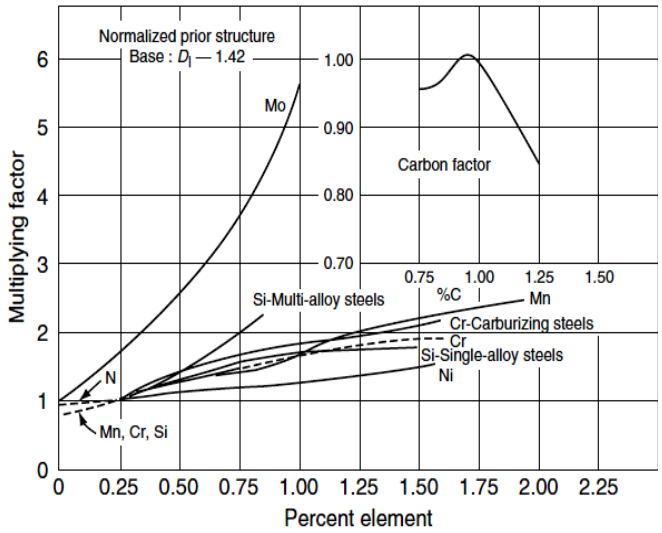



Figure 2.4: Multiplying factors for calculation hardenability of high carbon steels of prior normalized structure.

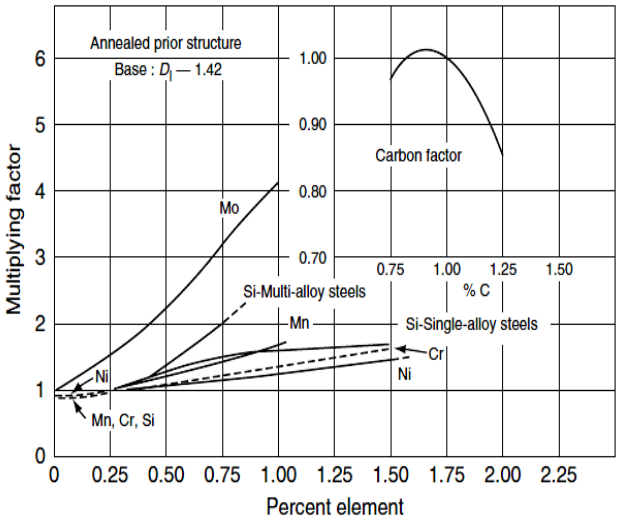



Figure 2.5: Multiplying factors for calculation of hardenability of high carbon steels of prior spheroidize-annealed structure.

The influence of austenitizing temperature on the specific hardenability effect is evident. The multiplying factors shown in Figs.2.6-9 were principally determined in compositions where only single alloy additions were made and that were generally pearlitic in initial transformation behavior. Consequently, these multiplying factors may be applied to the calculation of hardenability of all single alloy high carbon compositions and to those multi-alloyed compositions that remain pearlitic when quenched from these austenitizing conditions. This involves all analyses containing less than 0.15% Mo and less than 2% total of Ni plus Mn and also less than 2% Mn, Cr, or Ni when they are present individually. Of course, all of the factors given in the following figures also apply to the calculation of case hardenability of similar carburizing steels that are re-hardened from these temperatures following air cooling or integral quenching.

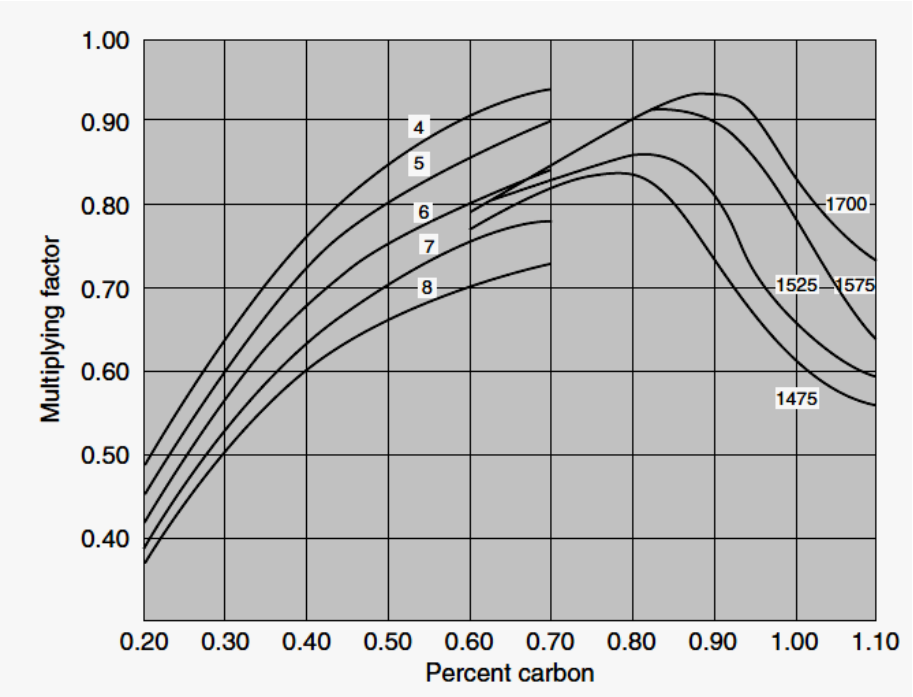



Figure 2.6: Multiplying factors for carbon at each austenitizing condition. Data plotted on the left hand side are data from Kramer for medium carbon steels with grain size variation from ASTM 4 to ASTM 8.

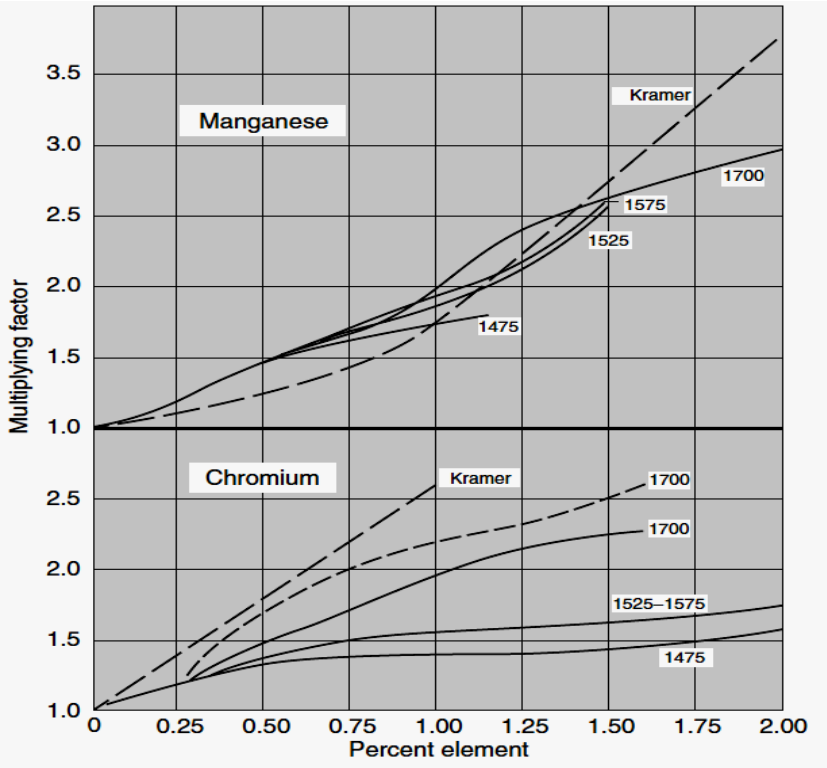



Figure 2.7: Effect of austenitizing temperature on multiplying factors for Mn and Cr at high carbon levels.

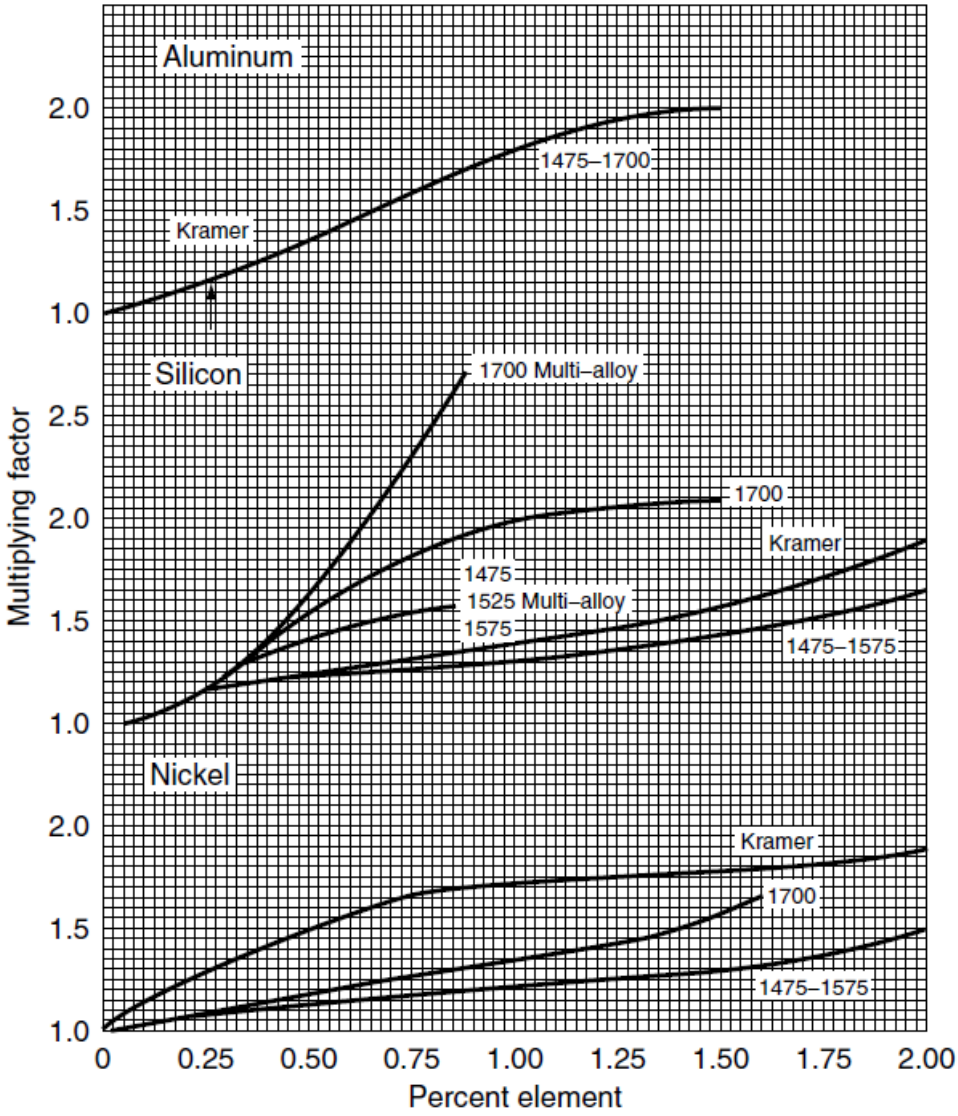



Figure 2.8: Effect of austenitizing temperature on multiplying factors for Al, Si and Ni at high carbon levels.

For steels containing more Mo, Ni, Mn, or Cr than the above percentages, the measured hardenability will always be higher than calculated with the single alloy multiplying factors because these steels are bainitic rather than pearlitic and also because synergistic hardenability effects have been found to occur between certain elements when present together. The latter effect was specifically noted between Ni and Mn, especially in steels made bainitic by the addition of 0.15% or more Mo and that also contained more than 1.0% Ni. The presence of synergistic effects precluded the use of individual multiplying factors for Mn and Ni, as the independence of alloying element effects is implicit in the Grossmann multiplying factor approach. This difficulty, however, was successfully surmounted by computing combined Ni and Mn factors as shown in Fig.2.9.

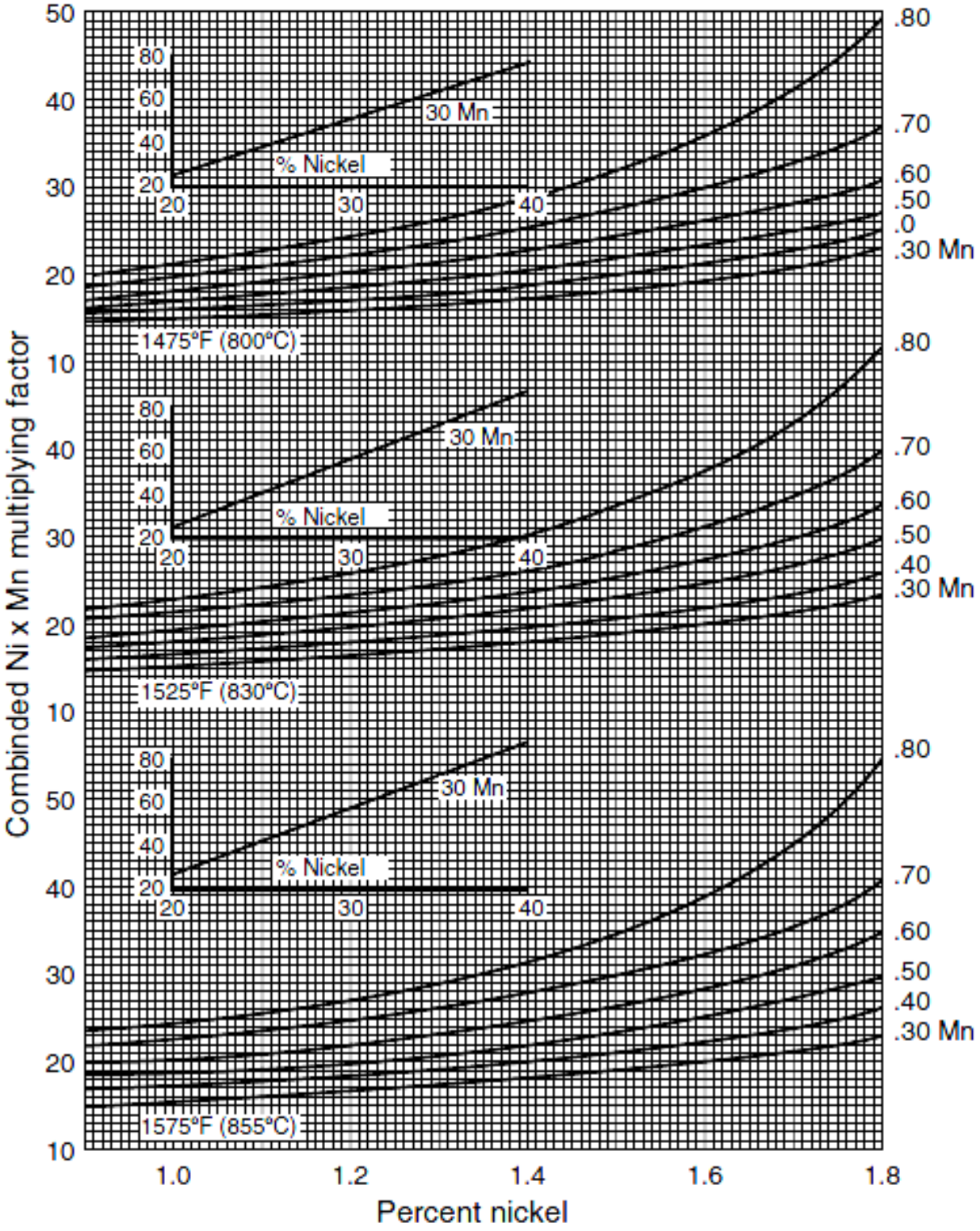



Figure 2.9: Combined multiplying factor for Ni and Mn in bainitic high-carbon steels quenched from 800 to 8558C, to be used in place of individual factors when composition contains more than 1.0% Ni and 0.15% Mo.

### 2.3.3 Jominy End Quench Hardenability Test

The end quench hardenability test developed by Jominy and Boegehold is commonly referred to as the Jominy test. It is used worldwide, described in many national standards and available as an international standard. This test has the following significant advantages:

a) It characterizes the hardenability of a steel from a single specimen, allowing a wide range of cooling rates during a single test.
b) It is reasonably reproducible.

The steel test specimen (25mm diameter x 100mm) is heated to the appropriate austenitizing temperature and soaked for 30min. It is then quickly transferred to the supporting fixture (Jominy apparatus) and quenched from the lower end by spraying with a jet of water under specified conditions as illustrated in Fig.2.10.

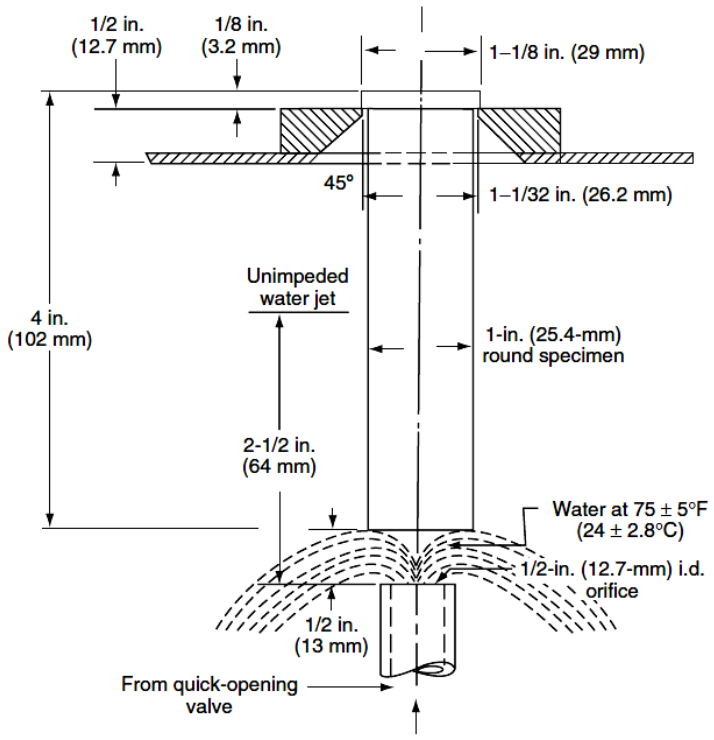



Figure 2.10: Jominy specimen and its quenching conditions for end quench hardenability test.

The cooling rate is the highest at the end where the water jet impinges on the specimen and decreases from the quenched end, producing a variety of microstructures and hardnesses as a function of distance from the quenched end. After quenching, two parallel flats, approximately 0.45mm below surface, are ground on opposite sides of the specimen and hardness values (usually HRC) are measured at 1/16 in. intervals from the quenched end and plotted as the Jominy hardenability curve (see Fig.2.11). When the distance is measured in millimeters, the hardness values are taken at every 2 mm from the quenched end for at least a total distance of 20

or 40 mm, depending on the steepness of the hardenability curve, and then every 10mm. On the upper margin of the Jominy hardenability diagram, approximate cooling rates at 700°C may be plotted at several distances from the quenched end.

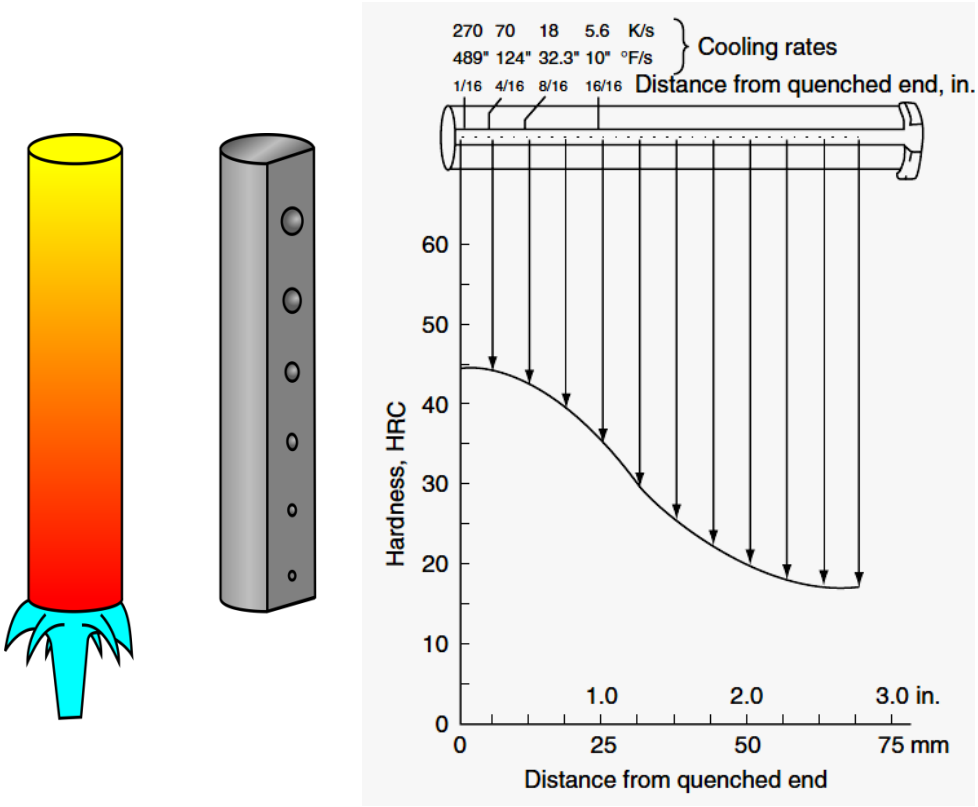



Figure 2.11: Measuring hardness on the Jominy specimen and plotting the Jominy hardenability curve.

### 2.3.4 Calculation of Jominy Curves from Chemical Composition

From more than half century long research on hardenability of steel, it was found that the influence of carbon depends on other alloying elements and also on the cooling rate, i.e., with distance from the quenched end (Jominy distance). Carbon starts at a Jominy distance of 0 with a multiplying factor of 50, while other alloying elements have the factor 0 at this distance. This implies that the hardness at a Jominy distance of 0 is governed solely by the carbon content. The influence of other alloying elements generally increases from 0 to values of their respective factors up to a Jominy distance of about 10mm. Beyond this distance, their influences are essentially constant. This led Just to propose a single expression for the whole test specimen, except for distances shorter than 6mm:

$$J_{6-80} = 95\sqrt{\mathrm{C}} - 0.00276E^2\sqrt{\mathrm{C}} + 20\mathrm{Cr} + 38\mathrm{Mo} + 14\mathrm{Mn} + 5.5\mathrm{Ni} + 6.1\mathrm{Si} + 39\mathrm{V} + 96\mathrm{P} - 0.81K - 12.28\sqrt{\mathrm{E}} + 0.898E - 13\mathrm{HRC}$$

where J is the Jominy hardness (HRC), E the Jominy distance (mm), K the ASTM grain size,

and the element symbols represent weight percentage of each. In the above equation, all alloying elements are adjusted to weight percent and it is valid within the following limits of alloying elements: C<0.6%; Cr<2%; Mn<2%; Ni<4%; Mo<0.5%; V<0.2%. Calculation of hardness at the quenched end (Jominy distance 0), using the equation for the maximum attainable hardness with 100% martensite is:

$$H_{\max} = 60\sqrt{\mathrm{C}} + 20\,\mathrm{HRC}, \quad \mathrm{C} < 0.6\%$$

Although the first equation was derived for use up to a distance of 80mm from the quenched end of the Jominy specimen, other authors argue that beyond a Jominy distance of 65mm the continuous decrease in cooling rate at the Jominy test cannot be ensured even for low alloy steels because of the cooling effect of surrounding air. Therefore, newer calculation methods rarely go beyond a Jominy distance of 40mm. Just found that a better fit for existing mutual correlations can be achieved by formulas that are valid for groups of similar steels. He also found that multiplying hardenability factors for Cr, Mn and Ni have lower values for case hardening steels than for structural steels for hardening and tempering. Therefore, separate formulas for case hardening steels were derived:

$$J_{6-40}(\text{case-hardening steels}) = 74\sqrt{\mathrm{C}} + 14\mathrm{Cr} + 5.4\mathrm{Ni} + 29\mathrm{Mo} + 16\mathrm{Mn} - 16.8\sqrt{E} + 1.386E + 7\mathrm{HRC}$$

and for steels for hardening and tempering,

$$J_{6-40}(\text{steels for hardening and tempering}) = 102\sqrt{\mathrm{C}} + 22\mathrm{Cr} + 21\mathrm{Mn} + 7\mathrm{Ni} + 33\mathrm{Mo} - 15.47\sqrt{E} + 1.102E - 16\mathrm{HRC}$$

### 2.3.5 Application of Hardenability Concept for Prediction of Hardness after Quenching

Jominy curves are the preferred methods for the characterization of steel. They are used to compare the hardenability of different heats of the same steel grade as a quality control method in steel production and to compare the hardenability of different steel grades when selecting steel for a certain application. In the latter case, Jominy curves are used to predict the depth of hardening, i.e., to predict the expected hardness distribution obtained after hardening parts of different cross sectional dimensions after quenching under various conditions. Such predictions are generally based on the assumption that rates of cooling prevailing at different distance from the quenched end of the Jominy specimen may be compared with the cooling rates prevailing at different locations on the cross sections of bars of different diameters. If the cooling rates are equal, it is assumed that equivalent microstructure and hardness can be expected after quenching. The diagrams shown in Fig.2.12 have been developed for this purpose. These diagrams provide a correlation of equivalent cooling rates at different distances from the quenched end of the Jominy specimen and at different locations (center, half radius, three quarter radius, surface) on the cross section of round bars of different diameters. They are valid for the specified quenching conditions only. Fig.2.12 is valid only for quenching in water at an agitation rate of 1m/s and the diagram in Fig.2.13 is valid only for quenching in oil at an agitation rate of 1m/s.

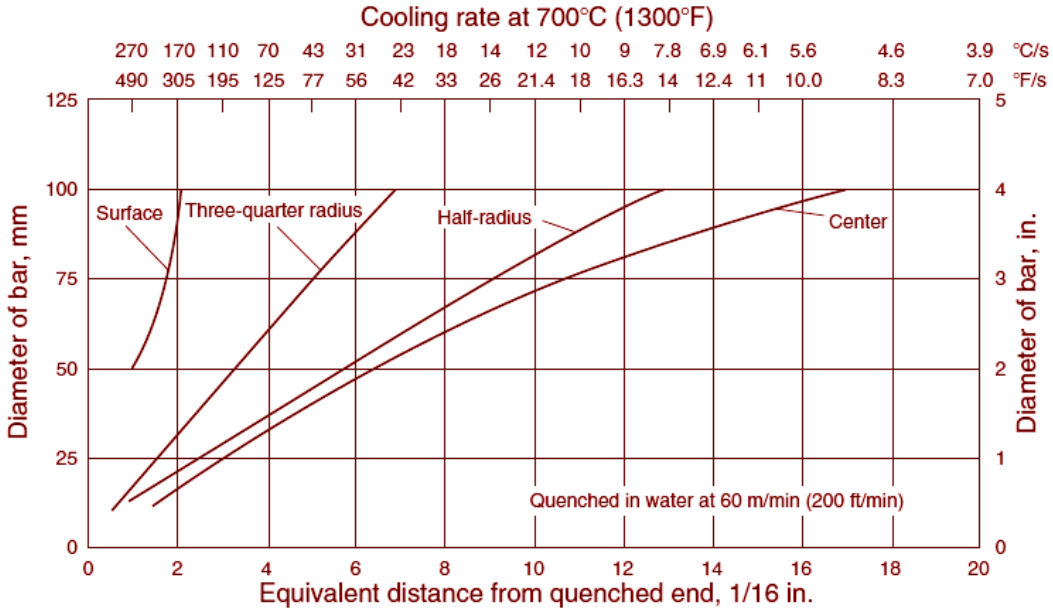

Cooling rate at 700°C (1300°F)
270 170 110 70 43 31 23 18 14 12 10 9 7.8 6.9 6.1 5.6 4.6 3.9 °C/s
490 305 195 125 77 56 42 33 26 21.4 18 16.3 14 12.4 11 10.0 8.3 7.0 °F/s
Surface
Three-quarter radius
Half-radius
Center
Quenched in water at 60 m/min (200 ft/min)
Diameter of bar, mm
Diameter of bar, in.
Equivalent distance from quenched end, 1/16 in.

Figure 2.12: Correlation of equivalent cooling rates at different distances from the quenched end of the Jominy specimen and at different locations on the cross section of round bars of different diameters, quenched in water agitated at 1m/s.

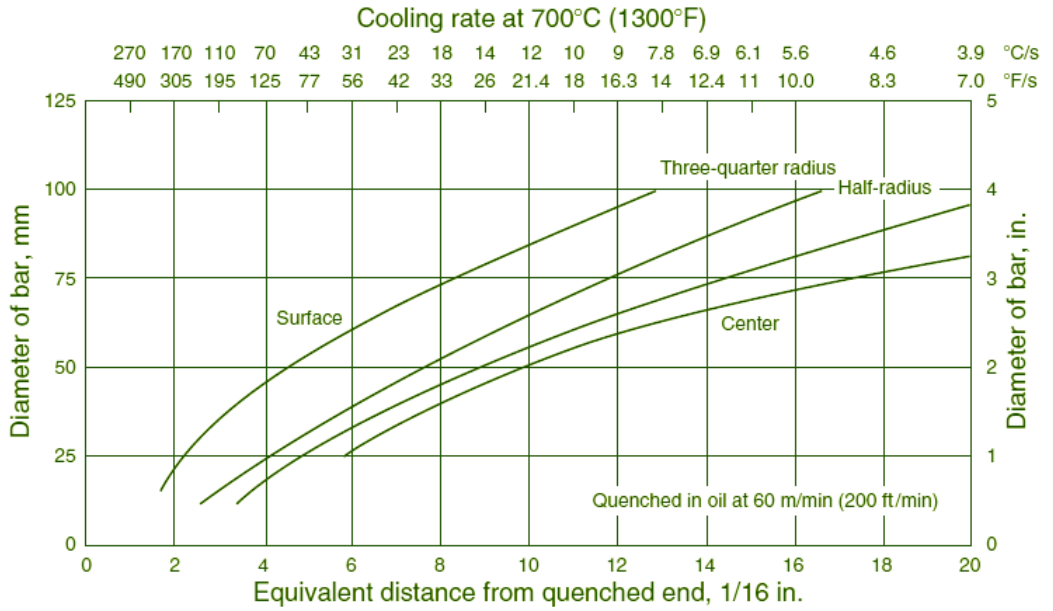

Cooling rate at 700°C (1300°F)
270 170 110 70 43 31 23 18 14 12 10 9 7.8 6.9 6.1 5.6 4.6 3.9 °C/s
490 305 195 125 77 56 42 33 26 21.4 18 16.3 14 12.4 11 10.0 8.3 7.0 °F/s
Three-quarter radius
Half-radius
Surface
Center
Quenched in oil at 60 m/min (200 ft/min)
Diameter of bar, mm
Diameter of bar, in.
Equivalent distance from quenched end, 1/16 in.

Figure 2.13: Correlation of equivalent cooling rates at different distances from the quenched end of the Jominy specimen and at different locations on the cross section of round bars of different diameters, quenched in oil agitated at 1m/s.

**Note: Practice to solve related problems**

## 2.4 Steel Selection Based On Hardenability

The selection of a steel grade (and heat) for a part to be heat treated depends on the hardenability that will yield the required hardness at the specified point of the cross section after quenching under known conditions. Because Jominy hardenability curves and hardenability bands are used as the basis of the selection, the method described here is confined to those steel grades with known hardenability bands or Jominy curves. This is true first of all for structural steels for hardening and tempering and also for steels for case hardening (to determine core hardenability).
If the diameter of a shaft and the bending fatigue stresses it must be able to undergo are known, engineering analysis will yield the minimum hardness at a particular point on the cross section that must be achieved by hardening and tempering. Engineering analysis may show that distortion minimization requires a less severe quenchant, e.g., oil. Adequate toughness after tempering (because the part may also be subject to impact loading) may require a tempering temperature of, e.g., 500°C. The steps in the steel selection process are as follows:

Step 1. Determine the necessary minimum hardness after quenching that will satisfy the required hardness after tempering. This is done by using a diagram such as the one shown in Fig.2.14. For example, if a hardness of 35 HRC is required after hardening and then tempering at 500°C at the critical cross sectional diameter, the minimum hardness after quenching must be 45 HRC.

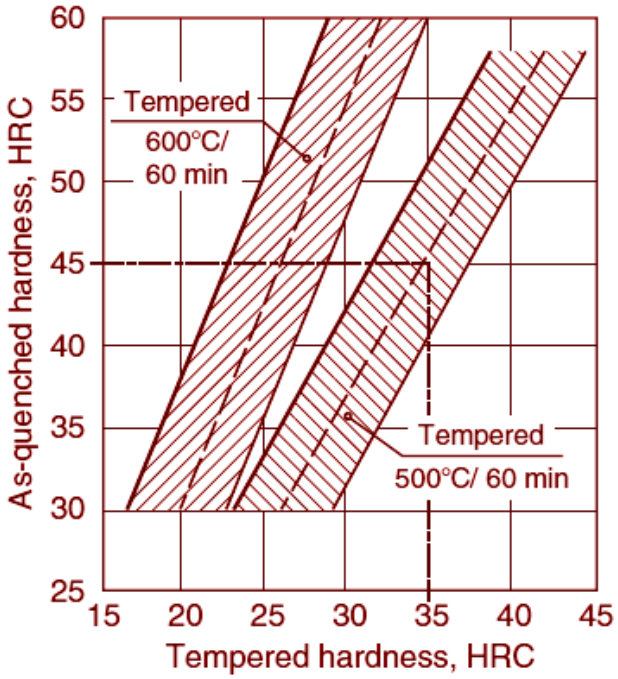



Figure 2.14: Correlation between the hardness after tempering and the hardness after quenching for structural steels (according to DIN 17200).

Alternatively, if the carbon content of the steel and the percentage of as quenched martensite at the critical point of the cross section is known, then by using a diagram that correlates hardness with percent carbon content and as quenched martensite content (see Fig.2.15), the as quenched hardness may then be determined. If 80% martensite is desired at a critical position of the cross section and the steel has 0.37% C, a hardness of 45 HRC can be expected. Figure 2.15 can also be used to determine the necessary carbon content of the steel when a particular percentage of martensite and a particular hardness after quenching are required.

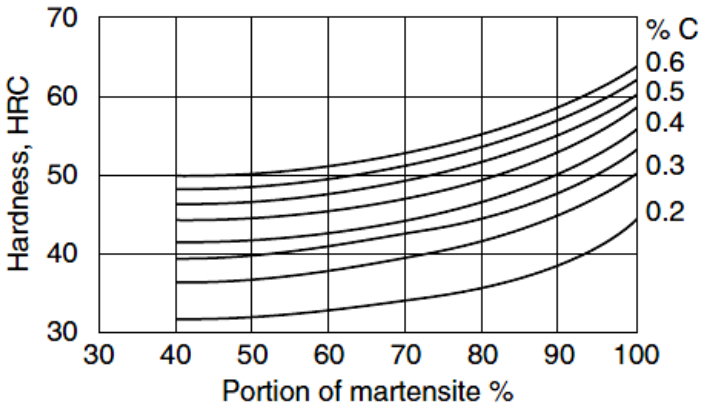



Figure 2.15: Correlation between as quenched hardness, carbon content and percent martensite.

Step 2. Determine whether a certain steel grade (or heat) will provide the required as quenched hardness at a critical point of the cross section. For example, assume that a shaft is 45mm in diameter and that the critical point on the cross section (which was determined from engineering analysis of resultant stresses) is three fourths of the radius. To determine if a particular steel grade, e.g., AISI 4140H, will satisfy the requirement of 45 HRC at (3/4)R after oil quenching, the diagram shown in Fig.16a should be used. This diagram correlates cooling rates along the Jominy end-quench specimen and at four characteristic locations (critical points) on the cross section of a round bar when quenched in oil at 1m/s agitation rate. Figure 2.16a shows that at (3/4) R the shaft having a diameter of 45mm will exhibit the hardness that corresponds to the hardness at a distance of 6.5/16 in. (13/32 in.) from the quenched end of the Jominy specimen.

Step 3. Determine whether the steel grade represented by its hardenability band (or a certain heat represented by its Jominy hardenability curve) at the specified distance from the quenched end exhibits the required hardness. As indicated in Fig.2.16b, the minimum hardenability curve for AISI 4140H will give a hardness of 49 HRC. This means that AISI 4140H has, in every case, enough hardenability for use in the shaft example above.

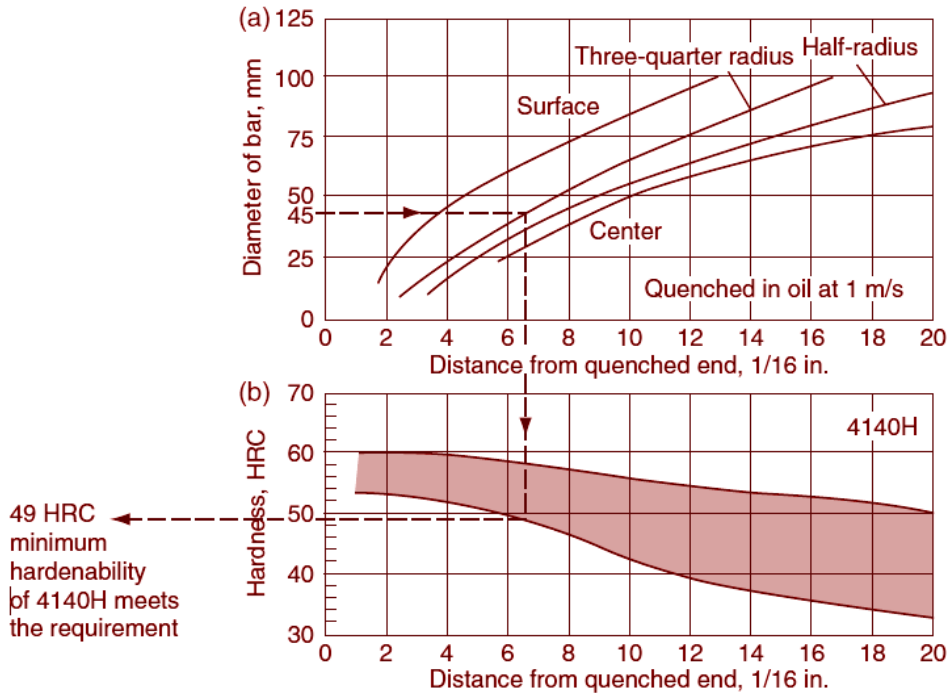



Figure 2.16: Selecting a steel of adequate hardenability (a) equivalent cooling rates (and hardness after quenching) for characteristic points on a round bar's cross section and along the Jominy end quench specimen and (b) hardenability band of AISI 4140H steel.

# Chapter Three

## Surface Hardening

### 3.1 Introduction

There are many applications that need a very hard and wear resistant surface, but ductile and tough core (Fig.3.1), which is almost impossible by traditional hardening methods. To satisfy these types of real life service requirements, special heat treatment technique that can induce hardness on the surface and sub-surface areas without significant change in core toughness became essential.

Figure 3.1: Some components that need surface hardening heat treatment.

Surface hardening is a process, which includes wide variety of techniques used to improve the wear resistance of parts without affecting the softer, tough interior of the part. This combination of hard surface and resistance to breakage upon impact is useful in parts such as shafts, gears, cams or rings, etc that must have a very hard surface to resist wear, along with a tough interior to resist the impact that occurs during operation. Furthermore, the surface hardening of steels has an advantage over through hardening because less expensive low carbon and medium carbon steels can be surface hardened without the problems of distortion and cracking associated with the through hardening of thick sections. There are distinctly different approaches for surface hardening as given below:

**I. Coatings**

a. Electrochemical plating, b. physical and chemical vapor deposition (electroless plating), c. ion mixing, etc.

**II. Hard Facing**

a. Fusion hard facing (welded overlay), b. Thermal spray (nonfusion bonded overlay).

**III. Diffusion Methods**

a. Carburizing, b. nitriding, c. carbonitriding, d. nitrocarburizing, e. boriding, f. titanium-carbon diffusion, g. Toyota diffusion process, etc.

**VI. Selective Hardening Methods**

a. Flame hardening, b. induction hardening, c. laser hardening, d. electron beam hardening, e. ion implantation, etc.

Surface hardening or modification by coating (electrochemical plating, vapour deposition, ion mixing, etc.), which is covered in surface engineering courses. So, this will not be discussed in this chapter. Surface hardening by hard facing includes the use of thin films, coatings or weld overlays is a part of welding, where it has been discussed. Films, coatings and overlays generally become less cost effective as production quantities increase, especially when the entire surface of work pieces must be hardened. The fatigue performance of films, coatings and overlays may also be a limiting factor, depending on the bond strength between the substrate and the added layer. Fusion welded overlays have strong bonds, but the primary surface hardened steels used in wear applications with fatigue loads include heavy case hardened steels and flame or induction hardened steels. Nonetheless, coatings and overlays can be effective in some applications. In the case of tool steels, for example, TiN and $Al_2O_3$ coatings are effective not only because of their hardness but also because their chemical inertness reduces wear and the welding of chips to the tool. Overlays can be effective when the selective hardening of large areas is required.

There are other surface hardening methods as diffusion methods and selective hardening methods. Diffusion methods modify the chemical composition of the surface with hardening species such as carbon, nitrogen or boron. This method is usually used for the components whose initial chemical compositions cannot ensure sufficient hardness level to restrict the wear rate under service. Diffusion methods allow effective hardening of the entire surface of a part and are generally used when a large number of parts are to be surface hardened. In contrast, selective surface hardening methods allow localized hardening. Here no change in the chemical compositions is made, which means that the alloying elements of the components must be capable inherently to harden the component to the optimum level. Selective hardening generally involves transformation hardening (from heating and quenching) without any change in chemical compositions. So, the parts to be surface hardened selectively must have suitable chemical compositions with proper hardenability, e.g. plain carbon steel having less than 0.25% carbon has a very poor hardenability. So, this steel is not a good choice for selective surface hardening.

Surface hardening by diffusion involves the chemical composition modification at the surface and sub-surface areas of the component. The basic process used is thermochemical rather than only chemical, because some heat is needed to enhance the diffusion of hardening species into the surface and sub-surface regions of the part. The depth of diffusion exhibits time-temperature dependence such that:

**Case depth ≈ K √Time**

where the diffusivity constant, **K**, depends on temperature, the chemical compositions of the steel and the concentration gradient of a given hardening species.

Methods of hardening by diffusion include several variations of hardening species (such as carbon, nitrogen or boron) and of the process method used to handle and transport the hardening species to the surface of the part. Process methods for exposure involve the handling of hardening species in various forms of media such as gas, liquid or ions. These process variations naturally produce differences in typical case depth and hardness, Fig.3.2.

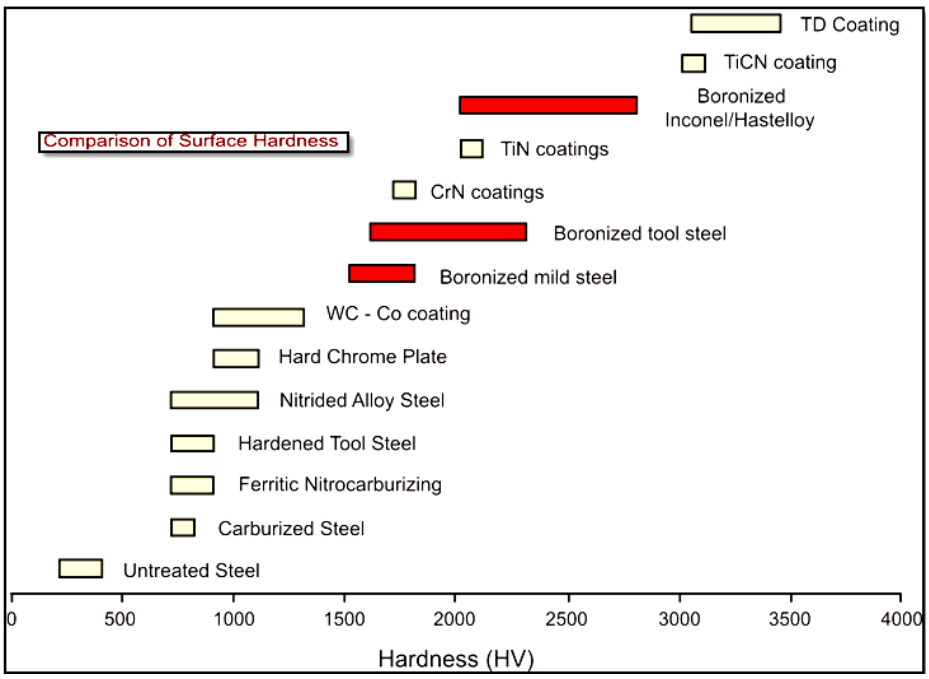



Figure 3.2: Hardness achieved from various surface hardening techniques.

One of the peculiar features of modified surface layers of structural materials is the occurrence of residual stresses therein. Residual stresses in surface hardened objects affect the performance characteristics and life of parts and tools, as well as the strength characteristics of both the coating itself and the substrate-coating system. The account of these stresses is required, since the residual stresses promote or inhibit fracture processes, depending on the sign, distribution and mode of loading. Therefore, a strong need exists to correctly estimate the level of residual stresses, to reveal the reasons for their occurrence, to establish the manufacturing factors and parameters of the surface architecture that influence their value. For example, electroplating of copper on substrate creates tensile residual stress in the coating (Fig.3.3).

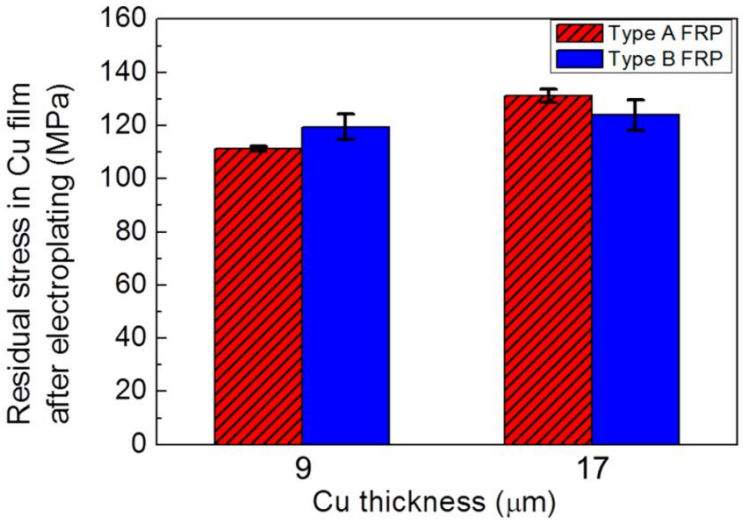



Figure 3.3: Residual stress created by electroplated copper.

On the other hand, a high residual compressive stress is created in the case of vacuum plasma TiN-coating on high speed steel (Fig.3.4) that provide enhanced crack growth resistance, wear resistance and corrosion resistance of surfaces.

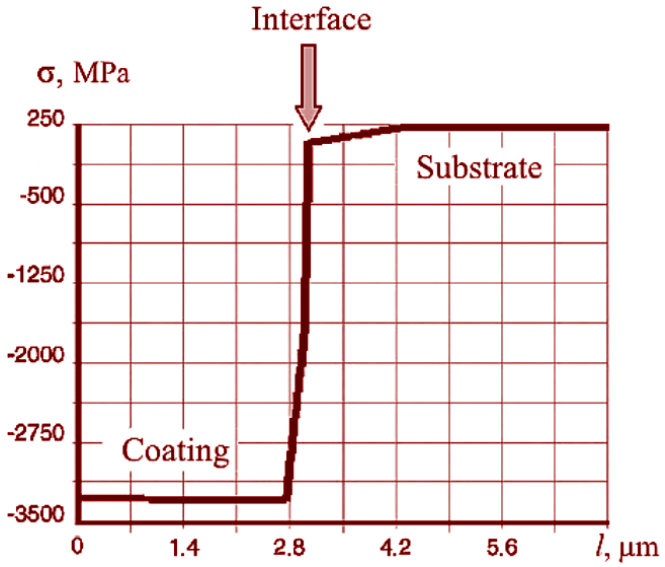



Figure 3.4: Compressive residual stress created on high speed steel by TiN coating.

In this chapter some important diffusion (case hardening) and selective surface hardening methods will be discussed.

### 3.2 Surface Hardening by Changing Chemical Compositions (Case Hardening)

#### 3.2.1 Carburizing

Carburizing is a process of addition of carbon to the surface of low carbon steels at temperatures between 850 and 950°C (1560 and 1740 °F) at which carbon solubility in austenitic iron very high. After carbon diffusion up to the predetermined depth from the surface of the component,

hardening is accomplished. For hardening, the carbon diffused surface layer is quenched to form martensite so that a high carbon martensitic case with good wear and fatigue resistance is superimposed on a tough, low carbon steel core. Surface hardening by carburizing can be classified into three kinds: gas (atmospheric gas, plasma and vacuum carburizing), liquids (salt bath carburizing) or solid compounds (pack carburizing). In each of these three processes, certain chemicals and methods are used. Case hardness of carburized steels is primarily a function of carbon content. Increase in carbon content also increases the surface hardness in the as carburized part, Fig.3.5.

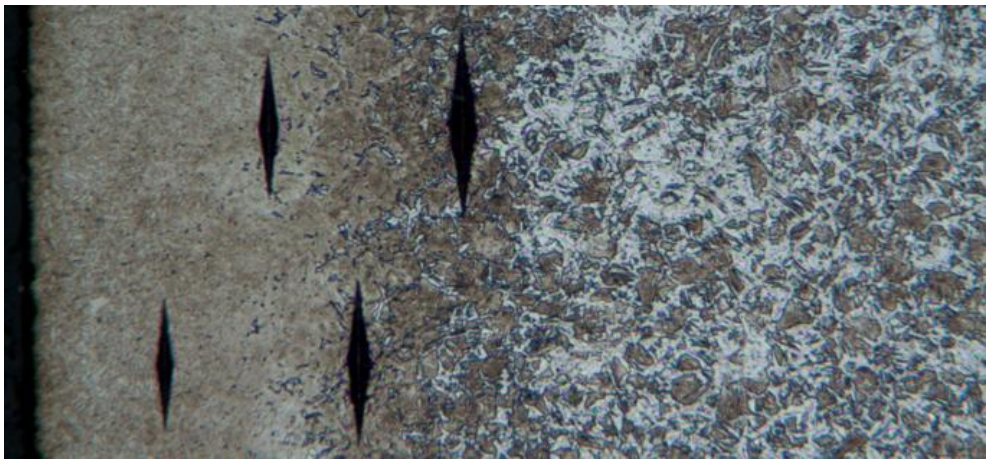


Figure 3.5: Variation in hardness of a carburized steel with carbon content.

However, the increase in surface hardness due to increase in carbon content only is not enough for most of the tribological applications. So, after carburizing, they are quenched. When the carbon content of the steel exceeds about 0.60%, additional carbon has no significant effect on hardness but does enhance hardenability (Fig.3.6). Case depth of carburized steel is a function of carburizing time and the available carbon (carbon potential) at the surface. When prolonged carburizing times are used for deep case depths, a high carbon potential produces a high surface carbon content, which may thus result in excessive retained austenite or free carbides. These two microstructural elements both have adverse effects on the distribution of residual stress in the case hardened part. Consequently, a high carbon potential may be suitable for short carburizing times but not for prolonged carburizing. Selection of carbon potential also depends on the carburizing response of the particular steel.

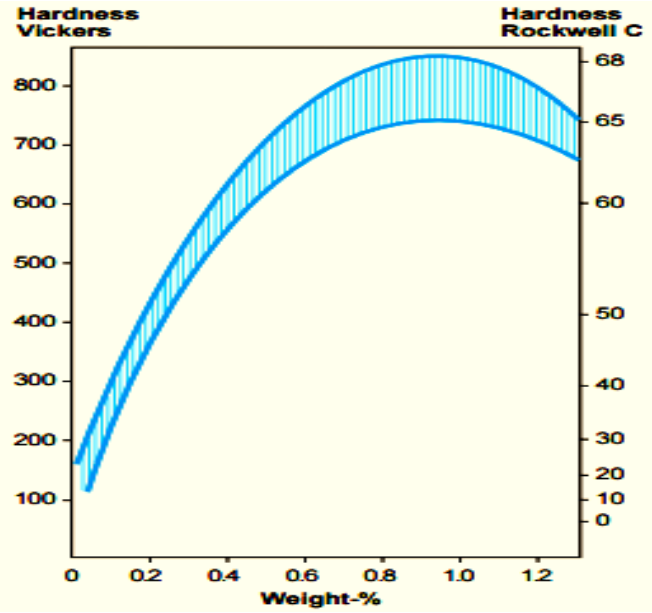


Figure 3.6: Effect of carbon content on the hardness of carburized and quenched steel.

### 3.2.2 Pack Carburizing

In pack carburizing, the media is in solid condition. This type of case hardening is applied where the chemical compositions of low carbon steel (0.1-0.25%C) is changed. For the solid carburizing the following solid ingredients may be used:

**Charcoal: 30-32%**
**Coke: 30-32%**
**Sodium Carbonate: 2-3%**
**Barium Carbonate: 10-12%**

Carburizing in solid media involves packing the workpieces into heat resisting boxes (Fig.3.7) by which the distance between them is maintained at least by 50mm, whereby causing diffusion of carbon rich material into the specimen surface by heating above the transformation temperature range of 900-950$^{o}$C. At this high temperature, the steel part is held in contact with a carbonaceous material for a specific period of time.

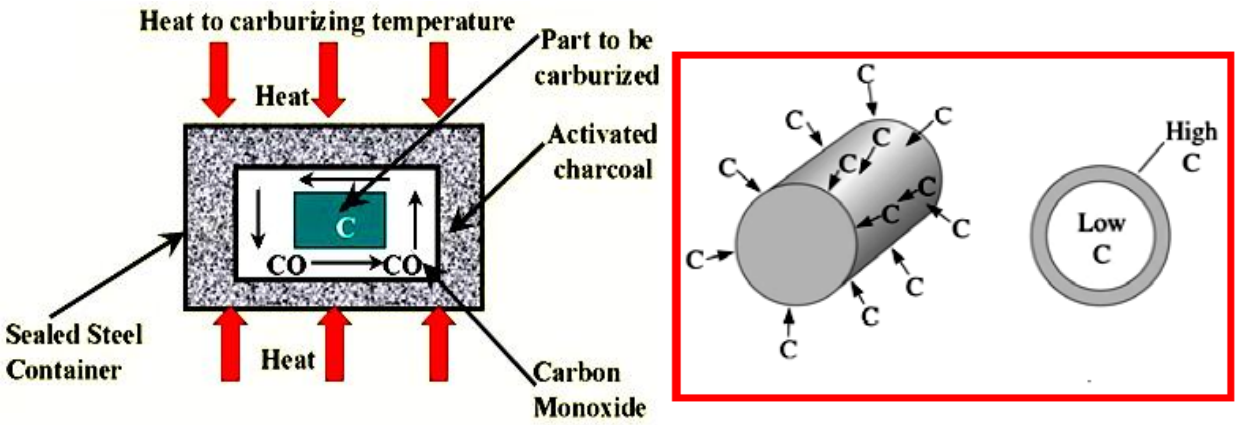



Figure 3.7: Pack carburizing technique and carburized case after carbon addition.

The charcoal is treated with an activating chemical such as barium carbonate ($BaCO_3$) that promotes the formation of carbon dioxide ($CO_2$). This gas in turn reacts with the excess carbon in the charcoal to produce carbon monoxide CO. Carbon monoxide reacts with the low carbon steel surface to form atomic carbon which diffuses into the steel. Carbon monoxide supplies the carbon gradient that is necessary for diffusion. The carburizing process does not harden the steel. It only increases the carbon content to some predetermined depth below the surface to a sufficient level to allow subsequent quench hardening. The overall chemical reactions that take place during solid carburizing method are given below:

$$BaCO_3 = BaO + CO_2$$
$$CO_2 + C = 2CO$$
$$2CO + 3Fe = Fe_\gamma C + CO_2$$

As the atomic carbon accumulates on the steel surface and diffuses inside it, the dissolved carbon concentration at the surface remains to the highest level. With distance from the steel surface, carbon concentration gradually decreases and at a certain depth there will be no change in carbon content. As a result, depending on the time of carburizing and/or concentration of carbon at the outer portion, from surface toward the core (where no concentration is changed) the microstructures will be gradually different, e.g. hypereutectoid, eutectoid, medium carbon and then core microstructure, Fig.3.8.

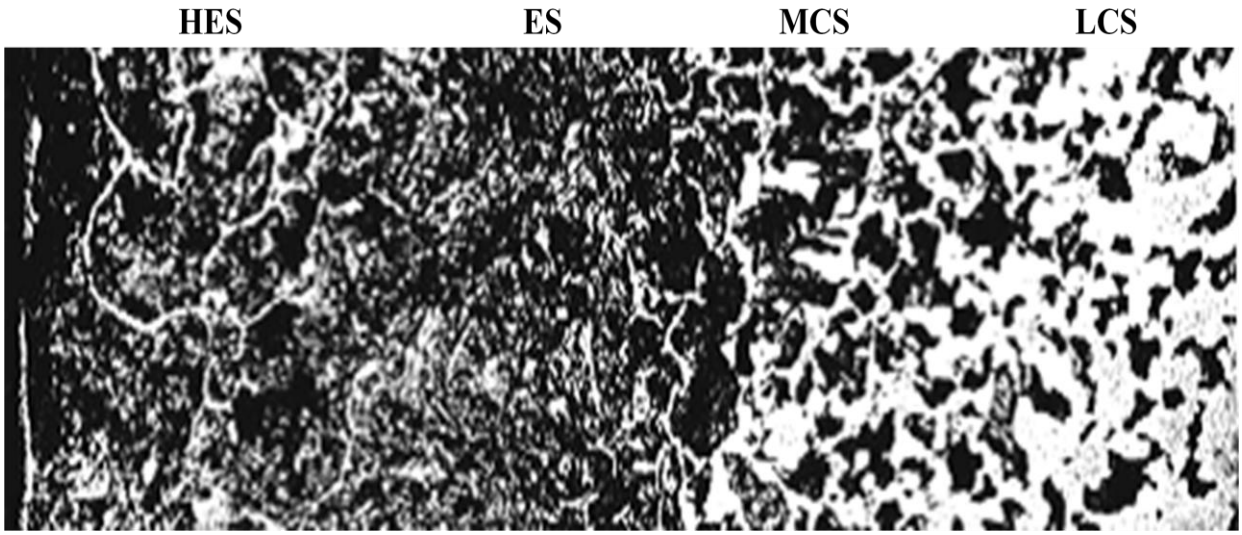



Figure 3.8: Variation in carbon content from surface to the core of a carburized steel.

### 3.2.3 Gas Carburizing

While the basic principle of carburizing has remained unchanged since it was first introduced, the methodology has gone through continuous evolution. Pack carburizing, although effective in introducing carbon, this method is exceedingly slow and as the production demand grew, a new method using a gaseous atmosphere was developed. In gas carburizing, the parts are surrounded by a carbon bearing atmosphere that can be continuously replenished so that a high carbon potential can be maintained, Fig.3.9. While the rate of carburizing is substantially increased in the gaseous atmosphere, the method requires the use of a multicomponent atmosphere whose composition must be very closely controlled to avoid deleterious side effects, for example, surface and grain boundary oxidation. Despite this increased complexity, gas carburizing has become the most effective and widely used method for carburizing steel parts in high volume.

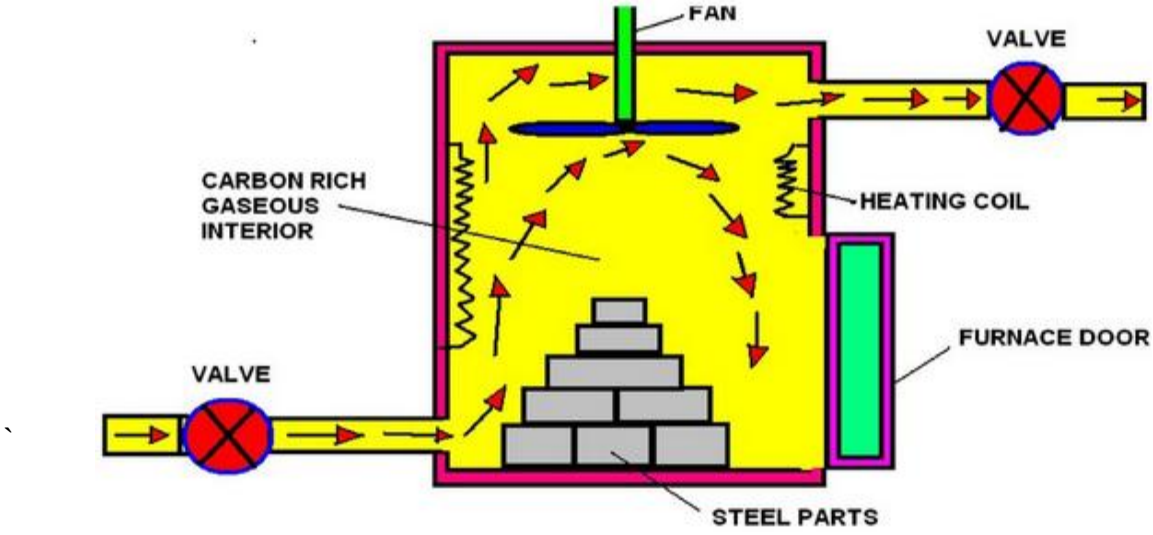



Figure 3.9: A typical setup for gas carburizing.

From a thermodynamic standpoint, the generation of the carburizing atmosphere is a rather complex process involving the interaction of numerous gases. Endothermic carburizing atmospheres consist of a mixture of carburizing agents (CO, $CH_4$) and decarburizing ($CO_2$, $H_2O$) agents, the ratio of which determines the carburizing potential in the furnace. As the driving force for carburizing is determined by the gradient between the carbon potential in the atmosphere and carbon at the steel surface, it is imperative to maintain a high carburizing potential throughout the whole process. Endothermic gas is most commonly produced by mixing air and natural gas in a fixed proportion, where the ratio may range from 2.5 to 5. The carrier gas entering the furnace is composed of CO, $CO_2$, $CH_4$, $H_2$, $H_2O$ and $N_2$. It has been estimated that nearly 180 chemical reactions occur simultaneously in the carburizing atmosphere, among which, only the following three reactions are important and determine the rate of carbon transfer from the carburizing atmosphere to the steel surface:

$$\mathbf{2CO \rightarrow C_{(\gamma\text{-}Fe)} + CO_2}$$
$$\mathbf{CH_4 \rightarrow C_{(\gamma\text{-}Fe)} + 2H_2}$$
$$\mathbf{CO + H_2 \leftrightarrow C_{(\gamma\text{-}Fe)} + H_2O}$$

While carburizing most rapidly proceeds by CO molecule decomposition, by products of the carburizing reactions ($CO_2$ and $H_2O$) act as decarburizing agents. The presence of $CO_2$ even in small quantities requires a high CO concentration to balance this decarburizing action. Therefore, for the process to proceed further, these decarburizing species must be reduced. The carburizing potential in the furnace is determined by the atmosphere gas composition. Accurate carbon potential calculation requires not only adequate measurement of the gas constituents (CO, $CH_4$, $CO_2$, $H_2O$) in the furnace but also representative sampling locations where the constituents are analyzed.

The mass transfer mechanism during gas carburizing is a complex phenomenon which involves three distinct stages: 1) carbon transport from the atmosphere to the steel surface, 2) surface chemical reactions and 3) diffusion of the absorbed carbon atoms towards the bulk of the steel down the chemical potential gradient. Total carbon transfer from the atmosphere to the steel is thus determined by the limiting process, which kinetically becomes the rate controlling stage of carburizing. Following Fig.3.10 schematically shows the mechanisms of carbon transfer during carburizing and the primary control parameters: the mass transfer coefficient (β) defining carbon atoms flux (J) from the atmosphere to the steel surface and the coefficient of carbon diffusion in steel (D) at austenitizing temperatures.

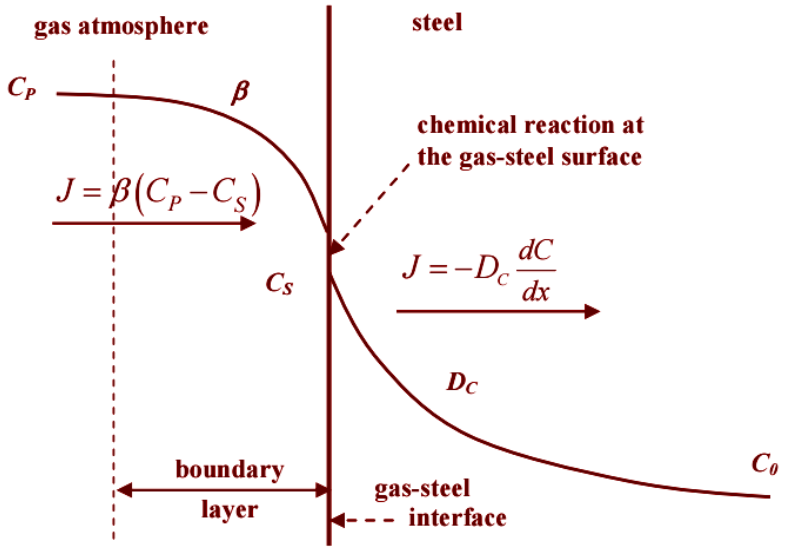



Figure 3.10: Distribution and mechanism of carbon transfer during carburizing.

Considering kinetics of the process, the maximum carburization rate is obtained when the carbon transfer from the atmosphere is equal to or greater than the carbon diffusion rate in the solid state. Such a diffusion controlled process has no deficiency of carbon supplied to the interface for its further transport into the solid; an assumption of constant surface carbon content may then be justified. In practice, however, the nonequilibrium carbon transfer from the atmosphere to the solid boundary including surface reaction is often reported to be the rate limiting factor especially at the start of the carburizing process. After this initial stage, the process becomes mixed controlled.

**Advantages of gas carburization:**

1) In gas carburization, the surface carbon content as well as the case depth can be accurately controlled.
2) It gives more uniform case depth.
3) It is much cleaner and more efficient method than pack carburizing.
4) Total time of carburization is much less than the pack carburization.

**Disadvantages of gas carburizing:**

1) Furnace and gas generator are expensive.
2) Trays are expensive.
3) Greater degree of operating skill is required.
4) Handling of fire hazards and toxic gases is difficult.

### 3.2.4 Vacuum Gas Carburizing

In efforts required to simplify the atmosphere, carburizing in an oxygen free environment at very low pressure (vacuum carburizing) has been explored and developed into a viable and important alternative. Although the furnace enclosure in some respects becomes more complex, the atmosphere is greatly simplified. A single component atmosphere consisting solely of a simple gaseous hydrocarbon, for example, methane or acetylene, may be used. Furthermore, because the parts are heated in an oxygen free environment, the carburizing temperature may be increased substantially without the risk of surface or grain boundary oxidation. The higher temperature permitted increases not only the solid solubility of carbon in the austenite but also its rate of diffusion, so that the time required to achieve the case depth desired is reduced, Fig.3.11. When carburizing at temperatures over 980°C), properly engineered steel chemistries are recommended to mitigate the potential for grain coarsening.

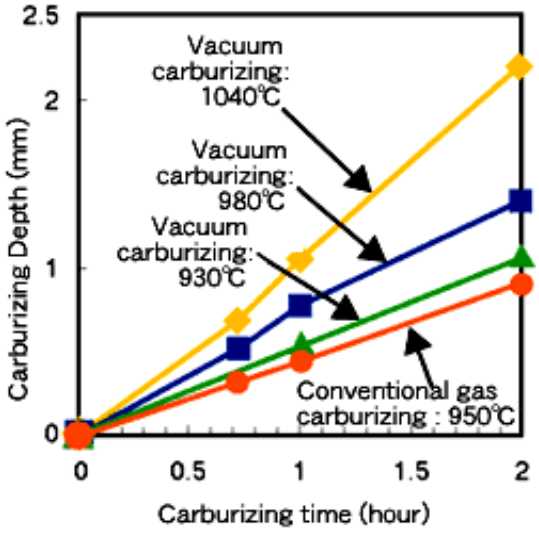



Figure 3.11: Effect of gas carburizing temperature on the depth of carburized layer.

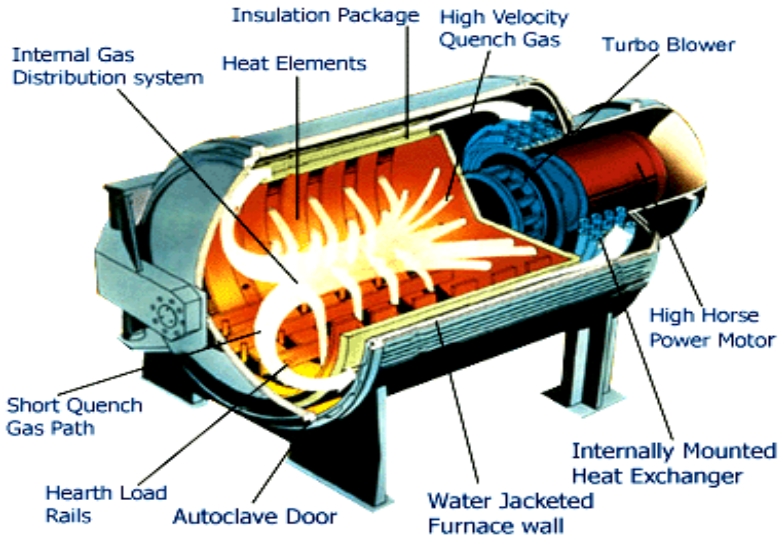



Figure 3.12: Vacuum gas carburizing furnace.

The vacuum carburizing furnace is a close chamber air tight furnace, Fig.3.12. Here, work pieces are placed in the closed chamber, the door is then closed and high level of vacuum is created inside the furnace. The steps are shown in the diagram presented in Fig.3.13.

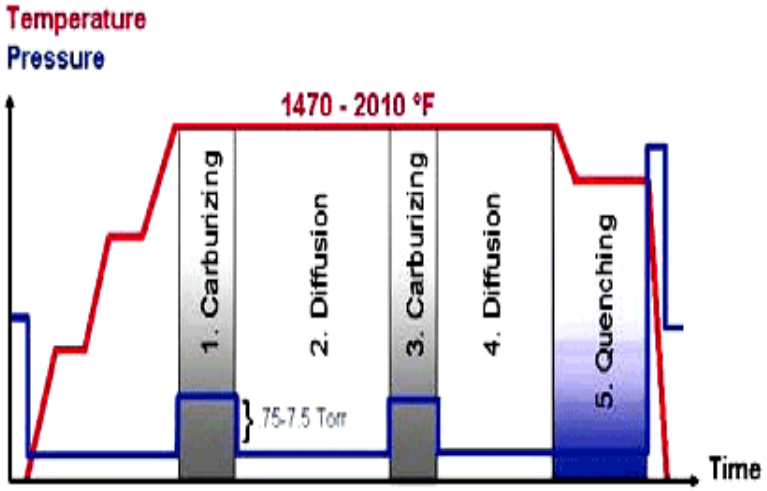



Figure 3.13: Schematic diagram showing various steps in vacuum gas carburizing.

Heating is then started and after achieving the proper carburizing temperature, carburizing media (propane or acetylene) is introduced with close control. Small quantities of carburizing gas are introduced in the hot zone and are drawn-off by the vacuum pumps. Process parameters like temperature and gas flow are selected according to the parts requirements and are used for the process control. To achieve the specified carbon profile, the carburizing is done in alternating steps for carburizing and diffusion, followed by a final diffusion step. Here it is to be mentioned that acetylene offers better carbon efficiency compared to propane because of its instability and higher carbon content per mol of gas (as per Table 3.1 given below).

Table 3.1: Various gases for vacuum carburizing.

| **Thermal Decomposition During Vacuum Carburizing** | | |
|---|---|---|
| Carburizing Gas | Carbon Content | Carbon Yield |
| Methane $CH_4$ | 75 % | < 3 % |
| Propane $C_3H_8$ | 82 % | ~ 25 % |
| Acetylene $C_2H_2$ | 92 % | ~ 60 % |

Once the charge has been heated to the carburizing temperature under the neutral vacuum atmosphere, propane very rapidly undergoes 100% dissociation into carbon and hydrogen. Vacuum carburizing is characterized by a high carbon mass flow rate, which carburizes the surface layer to near the carbon saturation limit within a short treatment time. In the subsequent diffusion phase, no more carburizing gas is fed in, rather the existing carbon diffuses further into the steel in accordance with the diffusion law until the desired carbon profile has been attained. In contrast to protective gas carburizing, vacuum carburizing can be performed with substantially higher case carbon contents. The case carbon percentage is already over 1.3% after a short period of carburization. The higher case carbon content in vacuum carburizing results in shortened treatment times, even at the same carburizing temperature. Rise in carburizing temperature results in a further considerable time saving without surface or grain boundary degradation because of absence of oxygen or moisture.

Heat treatment with gas quenching has already been an established process for two or three decades in the field of full hardening. The enhanced quenching action achieved with gas pressures above 10 bar has allowed successful extension of gas quenching to the field of low alloyed tool steels, steels for hardening and tempering, antifriction bearing steels and case hardening steels. Case hardening in vacuum heat treatment systems with gas quenching offers many advantages to the users compared to conventional protective gas carburizing with oil quenching. Parts are clean and dry after treatment requiring no washers or management or disposal of liquid waste. **As a protective atmosphere,** vacuum can prevent case oxidation and eliminate toxic off-gases. So, this is a very green heat treatment process. The case hardening steel can be carburized up to its limit of solubility in the surface layer without any sooting occurring. The system technology also makes it possible to carburize at temperatures above 1000°C without surface or grain boundary oxidation.

Vacuum carburizing technology produces work with minimum distortion, the direct result of being cooled down using gas. Surface metallurgy is superior because the carburization process is carried out in a vacuum environment, Vacuum furnace systems provide "cold-to-cold" (cold work going in, cold work coming out) and fully automatic operation, which reduces the amount of operator involvement thus minimizing labor costs. Considering upstream and downstream costs) vacuum carburizing provides a total reduction of processing costs and is a natural fit in a lean manufacturing cell. An additional advantage is that vacuum furnace technology is a green manufacturing process with no negative impact on the environment. Operation at higher temperatures results in shorter carburizing cycles due to considerably higher diffusion coefficient. Both the increased amount of carbon in the carburizing atmosphere and faster diffusion are responsible for the increase in vacuum carburizing efficiency

### 3.2.5 Plasma Carburizing

Plasma (ion) carburizing is basically a vacuum process using glow discharge technology to introduce carbon bearing ions to the steel surface for subsequent diffusion. This process is effective in increasing carburization rates, because the process bypasses several dissociation steps that produce active soluble carbon. For example, because of the ionizing effect of the plasmas, active carbon for adsorption can be formed directly from methane ($CH_4$) gas. High temperatures can be used in plasma carburizing, because the process takes place in an oxygen free vacuum, thus producing a greater carburized case depth than both atmospheric gas and vacuum carburizing.

Plasma carburizing process is undertaken in a batch type vacuum furnace with an integral quenching tank (usually oil). The chamber is operated at a reduced pressure of 0.1 to 3kPa (2 to 3 Torr) and at a temperature of 950°C or less. The components are held at a negative DC voltage of 400-800V (Fig.3.14) and the furnace as the former to be cathode, whilst a hydrocarbon gas (methane or propane) diluted with nitrogen, hydrogen and argon is introduced into the chamber at a few litres per minute. A glow discharge plasma is produced as a layer surrounding the components. This plasma contains elemental carbon which diffuses into the components' surface. Once carburization is complete, the gas flow and plasma are stopped and the components are held at temperature in the vacuum to allow further diffusion of the carbon into the substrate. The components are slightly cooled to about 850-950°C before being quenched in a bath of oil. Case depths of 0.2 to 2mm are achieved with a hardness of about 700HV.

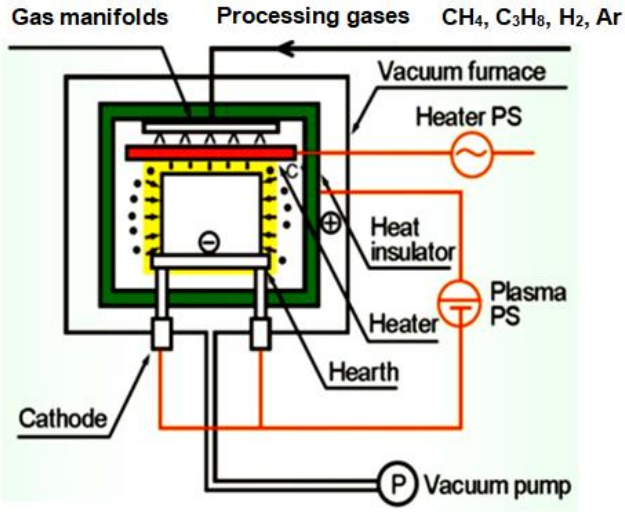



Figure 3.14: Schematic diagram showing the plasma carburizing setup.

The surface of the components can be cleaned in the chamber, prior to carburizing, by sputtering and hydrogen reduction of any oxides. 'Sooting', which often occurs in conventional gas carburizing, is avoided because the presence of carbon is restricted to the thin discharge layer. High capital cost of equipment limits the process to long production runs or short runs of

specialized, high value components. Some important features of plasma carburizing are given below.

(1) No oxidation takes place at grain boundaries, and the finished surface is clean and glossy.
(2) Even carburized layer is obtained because of plasma reaction, and no sooting is encountered.
(3) Due to fast carburizing rate and low temperature/short time treatment, no grain growth is observed and residual strain is very little.
(4) Carburizing of high concentration and the one into the hard-to-carburized materials, such as stainless steel, sintered metals, etc., can easily be made. •
(5) This is a pollution-free and energy saving processing. •

### 3.2.6 Carbonitriding

Carbonitriding is a case hardening process in which steel is heated in a gaseous atmosphere of such composition that carbon and nitrogen are absorbed simultaneously. The term carbonitriding is misleading because it implies a modified nitriding process. Actually carbonitriding is a modification of carburizing, and the name "nitro carburizing" would be more descriptive. The process is also known as dry cyaniding, gas cyaniding and nicarbing. The atmosphere used in carbonitriding generally comprises a mixture of carrier gas and ammonia. The carrier gas is usually a mixture of nitrogen, hydrogen, and carbon monoxide produced in an endothermic generator, as in gas carburizing. The presence of nitrogen in the austenite accounts for the major differences between carbonitriding and carburizing. Carbon and nitrogen make the austenite stable at lower temperatures and transforms more slowly on cooling. Carbonitriding therefore can be carried out at lower temperatures and permits slower cooling rates than carburizing in the hardening operation because of the lower temperature treatment.

### 3.2.7 Liquid Carburizing

Liquid carburizing is a method of case hardening steel by placing it in a bath of molten cyanide so that carbon will diffuse from the bath in to the metal and produce a case comparable to the one resulting from pack or gas carburizing. Liquid carburizing may be distinguished from cyaniding by the character and composition of the case produced. The cyanide case is higher in nitrogen and lower in carbon the reverse is true of liquid carburized cases. Low temperature salt baths (for thin case) usually contain a cyanide content of 20 percent and operate between 1550 and 1650°F. High temperature salt baths (deep case) usually have cyanide content of 10 percent and operate between 1650 and 1750°F.

**Adavatnges Liquid Carburizing**

1) Freedom from oxidation and sooting problems.
2) Uniform case depth and carbon content.
3) A rapid rate of penetration.

4) The fact that the bath provides high thermal conductivity, thereby reducing the time required for the steel to reach the carburizing temperature.

**Disadvantages Liquid Carburizing**

1) Parts must be thoroughly washed after heat treatment to prevent rusting.
2) Regular checking and adjustment of the bath.
3) Proper composition is necessary to obtain uniform case depth.
4) Some shapes cannot be handled because they either float or will cause excessive drag out of salt.
5) Cyanide salts are poisonous and require careful attention to satisfy the environmental regulations.

### 3.2.8 Design of Pack and Gas Carburizing

Carburization is one of the oldest industrial processes in which mass transport diffusion plays a major role. A source of carbon is provided at the surface of low carbon steel. The carbon diffuses into the steel at high temperatures usually 850 to 950°C, for time periods generally from a few hours to a day. A carbon gradient is produced in which the carbon content decreases from the surface into the steel. In the pack or gas carburizing process the carbon concentration at the surface of the steel is controlled by the $CO/CO_2$ ratio in the gas atmosphere, the temperature and the solubility of carbon in the steel. In the simplest carburization process, the carbon diffusion into any plain carbon steel at one temperature can be described by the Van-Ostrand Dewey solution to the diffusion equation:

$$\frac{C_C - C_S}{C_o - C_S} = \mathrm{erf}\left(\frac{X}{2\sqrt{Dt}}\right)$$

$C_S$ = Surface concentration of carbon, usually the maximum carbon content of γ at the temperature of carburizing. In general practice it is 1.3%C.

$C_o$ =Initial carbon level in Fe, usually <0.2%.

$C_C$ = Carbon concentration as a function of distance X in cm and time t in second

D = Diffusion coefficient for C in the γ phase in $m^2/s$, which is dependent of concentration on carbon concentration as well as temperature, Fig.3.15.

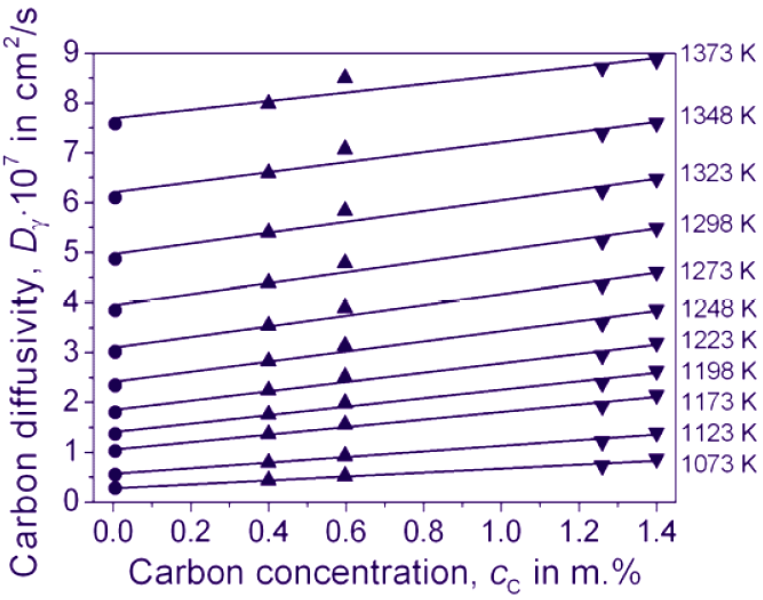



Figure 3.15: Effect of temperature on the carbon diffusivity in pure iron.

During carburization, the carbon concentration in iron is changed continuously. So, proper calculation of carburizing time at any particular temperature or carburization time for getting specific case depth for a particular component having certain initial carbon content is really very difficult job. From Figure 3.15, it is clear that the carbon diffusivity varies linearly with carbon concentration in iron. So, in the case of most steels, the carbon diffusivity in iron is assumed to be independent of carbon concentration and the average carbon diffusivity is calculated for most steel carburization process. The following approximated relationship can also be used depending on situation and available data:

$$\mathbf{lnD = lnD_o - } QRT \mathbf{\ or\ log\ D = logD_o - } Q/2.3RT$$

where $D_o$ is the frequency factor ($m^2/s$), Q is the activation energy (J/mol), T is temperature (K) and R is the universal gas constant (8.314 J/mol/K).

Table 3.2 contains the diffusion data for carbon in iron that is relevant to the carburization of steel. Since carburization usually takes place at temperatures within the FCC austenite phase field, the diffusion data for carbon in γ-iron is more relevant to this investigation. Since the FCC unit cell is more densely packed than the BCC unit cell, higher activation energy is required for the diffusion of carbon through austenite (γ) and the diffusion rate is lower in austenite than in ferrite (α) at the same temperature.

Table 3.2: Diffusion data for carbon in γ-iron and α-iron.

| *Diffusing element* | *Diffusing through* | *$D_o$ ($m^2.s^{-1}$)* | *Q ($kJ.mol^{-1}$)* | *D ($m^2 s^{-1}$) at 900°C* |
|---|---|---|---|---|
| Carbon | α-iron | $6.2 \times 10^{-7}$ | 80 | $1.7 \times 10^{-10}$ |
| Carbon | γ-iron | $2.3 \times 10^{-7}$ | 148 | $5.9 \times 10^{-12}$ |

Another term in the first equation the erf means error function, which is dependent on the value of distance from the reference point X. For simplification, it is again considered to be a fixed 0.5 for most of carburizing work.

Now, what should the definition of case depth? We know increase in carbon content increases the hardenability of the steel and hardness values of the hardened component, Fig.3.16. If a steel component is hardened, it needs tempering treatment which reduces the hardness values of the hardened steel to a wide scale depending on tempering temperature that has been shown in the earlier chapter. Another problem is the service condition, where the minimum hardness requirement under the surface of the carburized component is variable. However, for general purposes, there are two concepts regarding the case depths of carburized components. One is defined by carbon concentration, which is around 0.30%. This is measured by careful metallographic observation. In another way, it is defined by of hardness level of the as quenched component, which is around 30HRC scale (Fig.3.17), which is obtained from by hardness profile from hardened surface towards the core.

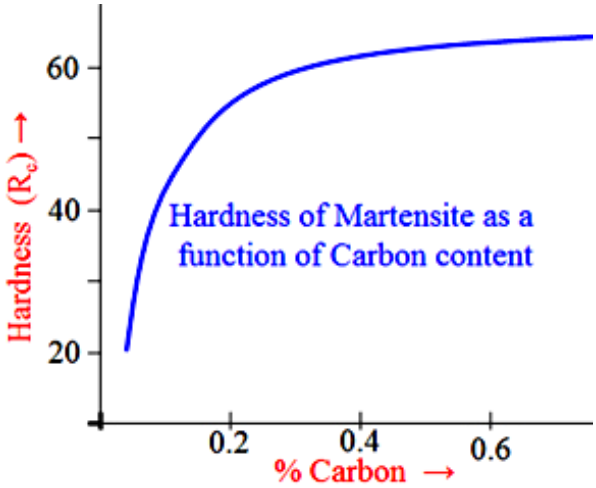



Figure 3.16: Variation of hardness of martensitic structures with carbon content.

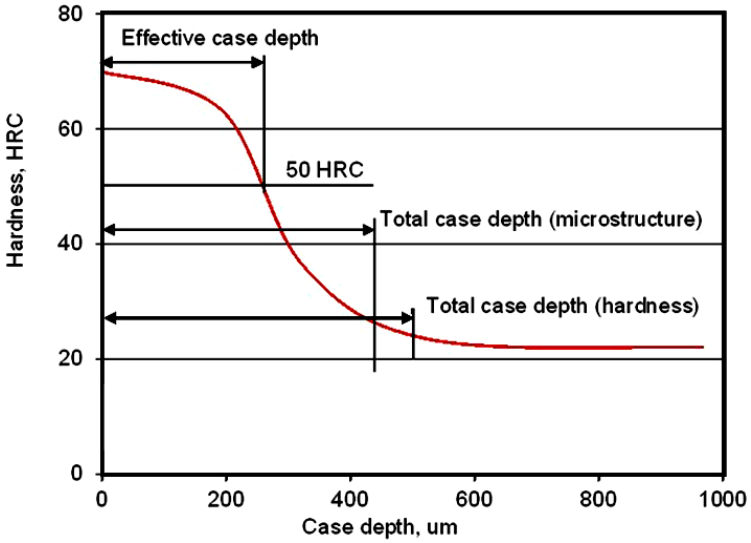



Figure 3.17: Measurement of case depth of carburized and hardened steel part.

**Problem 3.1:** A mild steel shaft has 0.15%C, which needs to be carburized by pack/gas carburizing method at 900°C. If the minimum carbon content at 2mm from the surface is to be 0.3%, what will be carburizing time?

**Solution:** We know

$$\frac{C_C - C_S}{C_o - C_S} = \text{erf}\left(\frac{X}{2\sqrt{Dt}}\right)$$

Here $C_S$ = 1.30, $C_o$ = 0.15, Erf = 0.5 and $C_C$ = 0.3

From Figure 3.15 D = $2.04 \times 10^{-7}$ cm$^2$/s = $2.04 \times 10^{-3}$ m$^2$/s. Now, by solving the above equation t will be around 41hrs. This indicates that pack carburizing is a very slow process.

### 3.2.9 Alloy Dependence of the Diffusion Coefficient of Carbon in Austenite

The prediction of carburization depths for case hardening represents the most important practical application of the diffusivity of carbon in austenite. Experimental data on multi-component iron based systems are rare. The general statement in the literature, however, is that the small amounts of maximal few wt.% of alloying elements, such as Cr or Si, typical of steels for case hardening do not significantly influence the carbon diffusion coefficient. On the other side, a noticeable dependence of the carbon diffusivity in austenite on the alloy composition is noticed, which is also supported by metal physics based analyses as well as software based analysis (*SimCarb).* As per the *SimCarb Diffusivity* model, carbon diffusion coefficient (CDC) of Fe-C alloys throughout the whole studied interval of temperatures (800-1300°C) and carbon concentrations (0.22-1.35%) has been presented precisely, Fig.3.18.

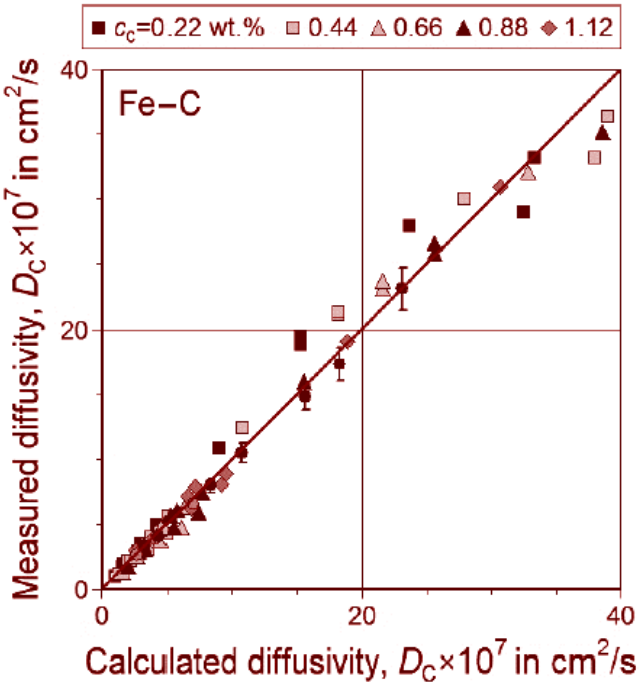



Figure 3.18: Correlation between the measured and calculated CDC values for the binary Fe–C alloys. The accuracy bars correspond to ±7% from the measured value.

The diffusivity of carbon in iron also temperature dependent, which can be calculated by using equation mentioned earlier or directly from the curve given in Fig.3.15. Utilization of experimental investigation data on the carbon diffusivity in the ternary alloys Fe-C-X*i* (X*i*=Cr, Mn, Mo, Ni, Si, Al, W, Co) with different carbon has been performed. The developed model allows to describe a slowing down of the diffusion of carbon owing to the carbide forming elements (Cr, Mn, Mo, Al, W), which reduce its activity in an austenite, as well as diffusion acceleration by elements (Ni, Co) raising the carbon activity. Additional alloying by Cr, Mn, Mo, Al and W results in an increase of the activation energy, whereas additions of Ni and Co reduces this energy. The effects of various alloying elements on the carbon diffusivities in iron are shown below in Fig.3.19 at different temperatures.

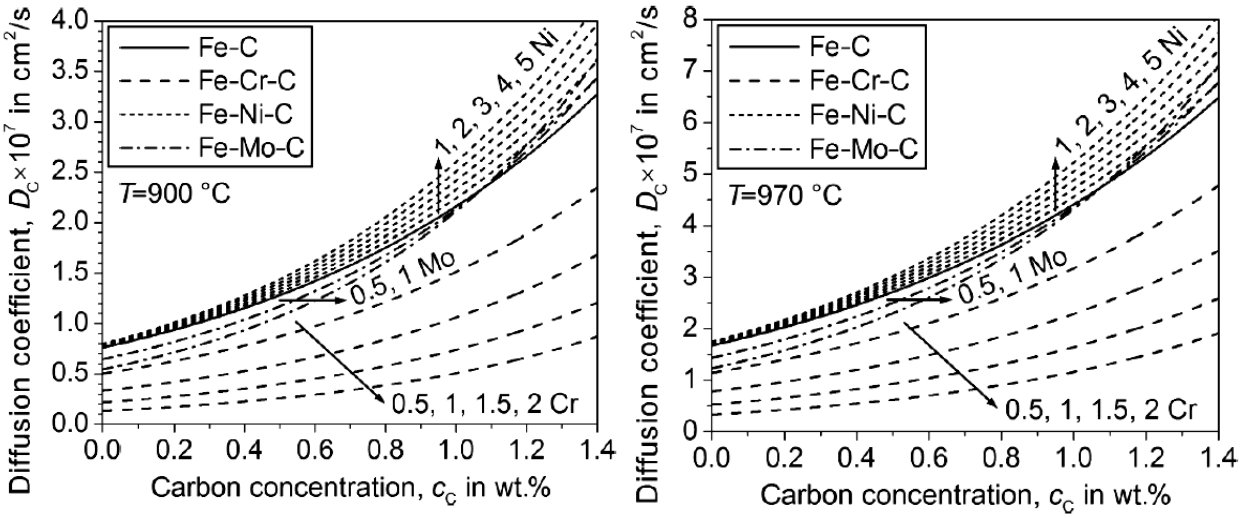



Figure 3.19: SimCarb Diffusivity prediction of the effect of typical Cr, Ni and Mo contents (in wt.%) on the concentration dependent diffusion coefficient of carbon in ternary austenite at 900 and 970°C.

Nickel and silicon are austenite stabilizers. The general tendency of these alloying elements is to increase the carbon diffusivity. Ni shows the expected effect in the whole temperature range relevant to carburizing (900 and 970°C). The predicted influence of Si is somewhat complex. At most common carburizing temperatures up to 980°C, Si greatly increases the diffusion coefficient of carbon in austenite. As per Fig.3.20 given below, a rise of over 20% and about 50% corresponds to usual alloying additions of 0.2 and 0.4 wt.% Si, respectively, at 900 and 970°C. A transition occurs around 1000 °C. At higher temperatures, a slight reversed effect on the carbon diffusivity, e.g. at 1050 °C -5% to +1% at 0.2 wt.% Si and -9% to +2% at 0.4 wt.% Si, Fig.3.20.

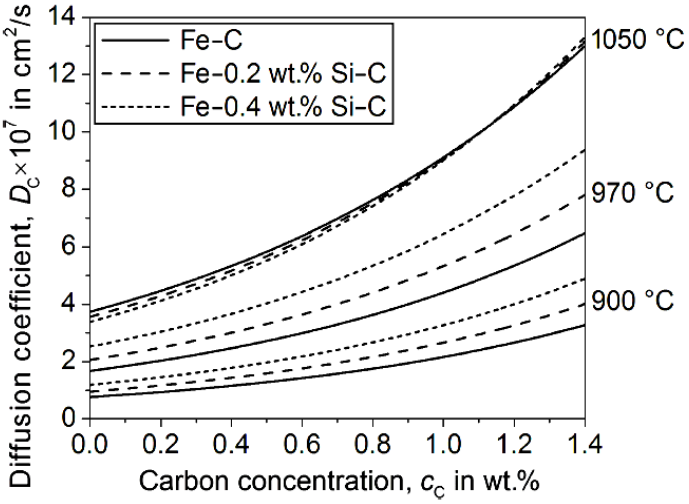



Figure 3.20: SimCarb Diffusivity prediction of the temperature dependent Si effect (typical lloying con-tents) on the carbon diffusion coefficient in Fe–C–Si austenite at 900, 970 and 1050

**Problem 3.2:** What will be the carburizing time if the carbon steel in Problem 1 is replaced by a low alloy steel having the same carbon content along with 1% Cr/1% Mo separately or in combination.

**Solution:** Find out the average value of D when 1%Cr is added, which is around $1.2 \times 10^{-3}$/s. Similarly find out the value of D when Mo is added singly. Calculate the percentage of diffusivity reduction, then carburizing time. Then find out the combined action of these two elements on D value as well as the carburizing time.

### 3.2.10 Hardening of Carburized Part

Case hardening typically consists of three steps. In the first step, work pieces are exposed to a carbon and/or nitrogen emitting environment. This increases the carbon and/or nitrogen percentage at the surface of the workpiece. The carbon profile and the penetration depth depend on the time at temperature, the amount of supplied carbon, the temperature and the kind of steel used. In the second phase, quenching (hardening) followed by takes place. This can be performed directly from the carburizing temperature (A in Fig.3.21). To have the targeted case depth, the austenite grains in the steel usually get coarsened because of long time exposure at high temperature. If there is possibility of cracking or warping due to coarse grains caused by this prolonged time of carburizing, then hardening cycle of type B might be followed. In this case, cooling below lower critical temperature causes transformation of coarse grained austenite to ferrite-pearlite structure and further reheating to above the lower critical temperature ensure fine grained austenite, especially at the surface and subsurface where high carbon content persists. In this condition, when quenched crack free much better hardened surface is expected.

Heat treatment schedule B cannot give guarantee of crack and/distortion free hardened component. Because, cracking or distortion control is not so straight forward process as it is influenced by so many parameters. In the case of complex part, in many instances, heat treatment schedule B may not be enough. In such cases, instead of directly quench in cold water to quench

in oil or in a warm bath. If this initiative cannot provide expected defect free component, we can practice heat treatment schedule C, where the carburized component is cooled slowly in the furnace. Then it is heated just above the upper critical temperature and held there for a while and then cooled in a suitable quenching media. This hardening module serves to diminish the highest stresses in the structure and to diminish the grinding crack sensitivity.

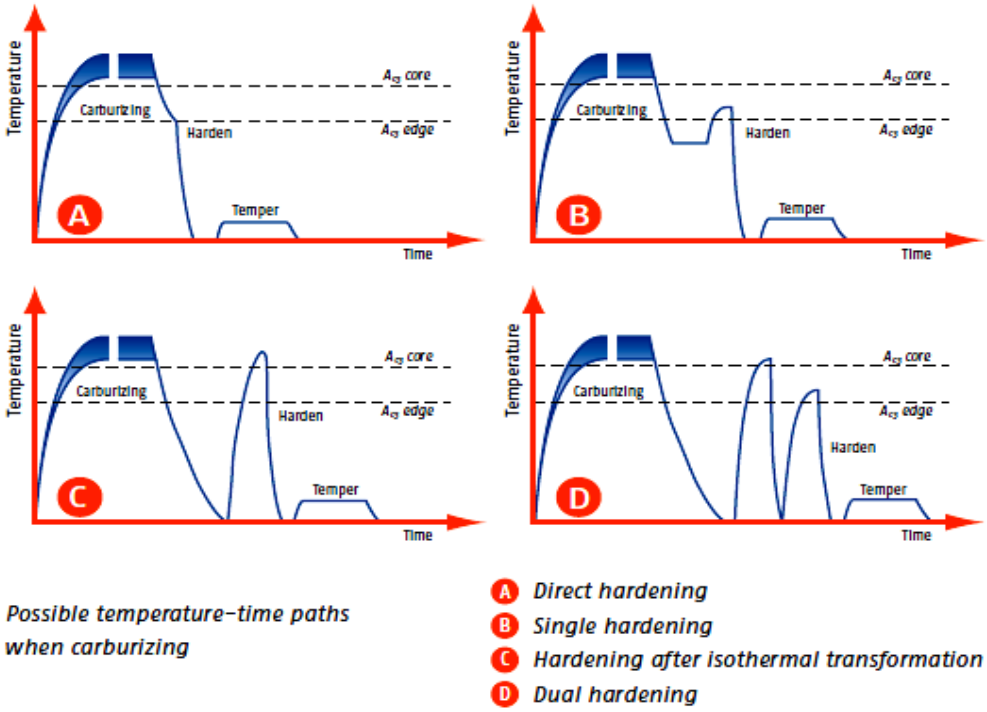



Figure 3.21: Various modules of hardening for carburized steel parts.

In some very complex cases where heat treatment module C is still not enough for defect free components, then we can try dual hardening route as shown in module D. Here carburized part is cooled slowly in the furnace, then reheated to just above upper critical temperature from which it is cooled in the quenching media. This step will ensure fine grain martensitic microstructures. This one is again heated to just above lower critical temperature, where only high carbon portion will be transformed to very fine grained austenite. If this partially transformed component is quenched then hardened case with relatively better toughness will be ensured. For all cases, after final hardening, proper tempering heat treatment must be incorporated. Here it is to be mentioned that heat treatment module selection from A to D, the costing will gradually increase. So, adoption of any module must be justified with price and service conditions of the component.

### 3.3 Nitriding

Nitriding is one type of case hardening method. First developed in the early 1900s, continues to play an important role in many industrial applications. Along with the derivative nitrocarburizing process, nitriding often is used in the manufacture of aircraft, bearings, automotive components, textile machinery and turbine generation systems. Though wrapped in a bit of “alchemical

mystery," it remains the simplest of the case hardening techniques. The secret of the nitriding process is that it does not require a phase change from ferrite to austenite, nor does it require a further change from austenite to martensite. In other words, the steel remains in the ferrite phase (or cementite, depending on alloy composition) during the complete procedure. This means that the molecular structure of the ferrite (body centered cubic or bcc, lattice) does not change its configuration or grow into the face centered cubic (fcc) lattice characteristic of austenite, as occurs in more conventional methods such as carburizing. Furthermore, because only free cooling takes place, rather than rapid cooling or quenching, no subsequent transformation from austenite to martensite occurs. Again, there is no molecular size change and more importantly, no dimensional change, only slight growth due to the volumetric change of the steel surface caused by the nitrogen diffusion. What can (and does) produce distortion are the induced surface stresses being released by the heat of the process, causing movement in the form of twisting and bending. Some nitrided components used in very high-tech applications are shown in Fig.3.22.

Figure 3.22: Some important nitrided components.

### 3.3.1 Metallurgical Considerations and Process Requirements

Nitriding is a ferritic thermochemical method of diffusing nascent nitrogen into the surface of steels and cast irons. This diffusion process is based on the solubility of nitrogen in iron, as shown in the iron-nitrogen equilibrium diagram (Fig.3.23).

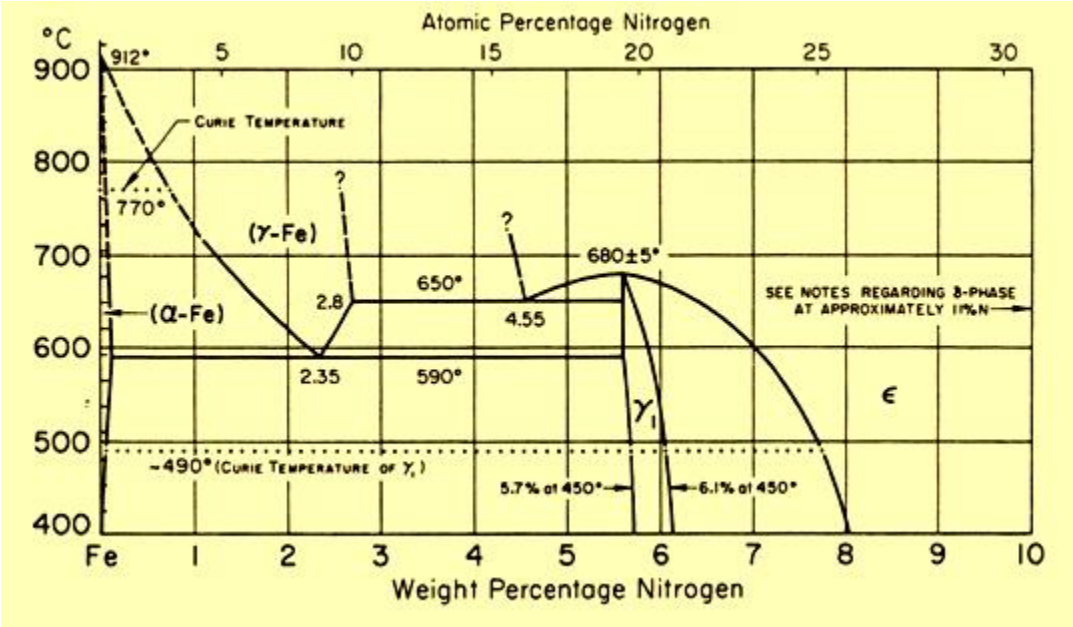



Figure 3.23: Fe-N binary phase diagram.

The solubility limit of nitrogen in iron is temperature dependent and at 450°C the iron base alloy will absorb 5.7 to 6.1% of N. If the temperature is increased beyond this level the N solubility level does not improve. This is strongly influenced by the carbon content of the steel, Fig.3.24. The greater the carbon content, the more potential for the epsilon has to form, which is very brittle in nature. As the temperature is further increased to the gamma prime phase temperature at 490°C (914 °F), the "window" or limit of solubility begins to decrease. Moreover, higher temperature nitriding might also cause more deformation and/or distortion. So, as per the equilibrium diagram it is clear that control of the nitrogen diffusion is the most critical task to make the process success.

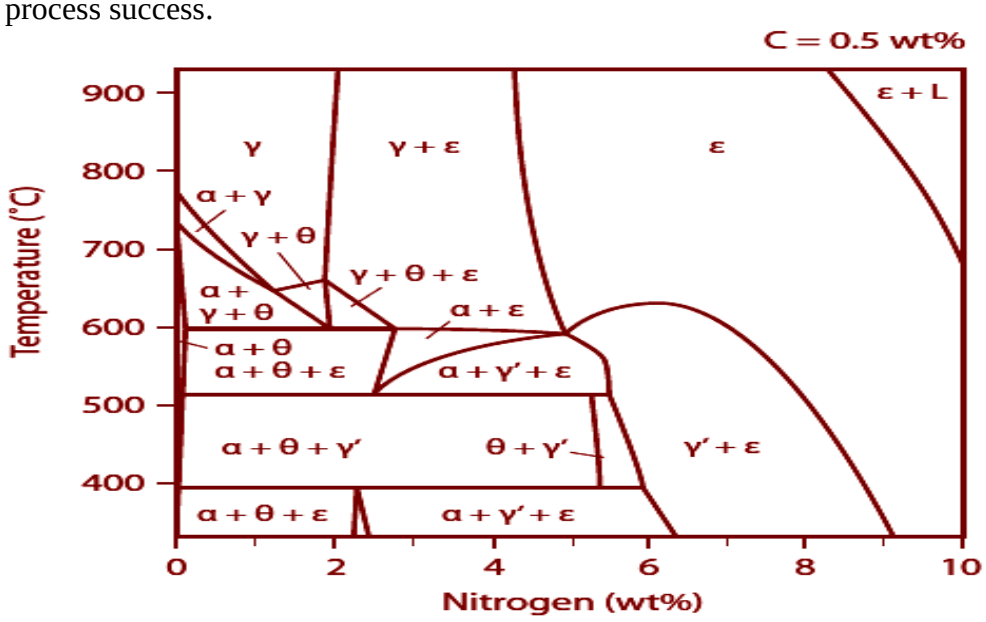



Figure 3.24: Fe-N phase diagram with 0.5%C.

If the nitriding temperature is too high, especially above the lower critical temperature excessive grain growth will take place. In this case surface hardness value might be deteriorated and there will be serious hardness gradient between case and the core, Fig.3.25. This high level of hardness gradient ultimately shortens the service life of the nitrided components. So, increase in nitriding temperature beyond this temperature means just increase in per unit production costing without any benefit.

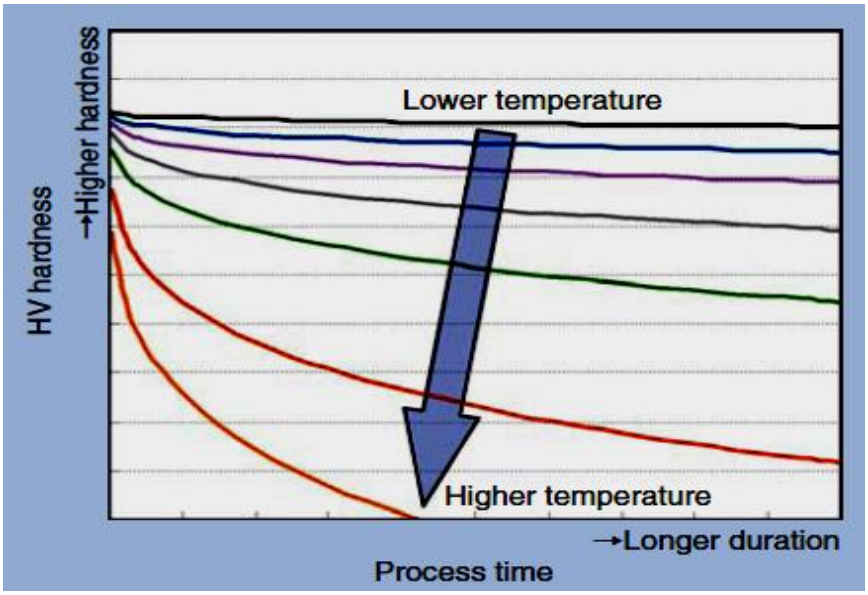



Figure 3.25: Effects of nitriding temperature on hardness gradient.

Nitrided steels are generally medium carbon (quenched and tempered) steels that contain strong nitride forming elements such as aluminum, chromium, vanadium, titanium and molybdenum. The most significant hardening is achieved with a class of alloy steels (nitralloy type). A typical composition of a nitralloy is given below.

| Typical Composition | C | Mn | Si | Cr | Mo | Al |
|---|---|---|---|---|---|---|
| | 0.40 | 0.60 | 0.30 | 1.60 | 0.35 | 1.20 |

When these steels are nitrided the aluminum forms AlN particles, which strain the ferrite lattice and create strengthening dislocations. Titanium and chromium are also used to enhance case hardness although case depth decreases as alloy content increases. Of the alloying elements commonly used in commercial steels, aluminum, chromium, vanadium, tungsten and molybdenum are beneficial in nitriding because they form nitrides that are stable at nitriding temperatures. Molybdenum in addition to its contribution as a nitride former also reduces the risk of embrittlement at nitriding temperatures. Other alloying elements such as nickel, copper, silicon and manganese have little, if any, effect on nitriding characteristics. Although at suitable temperatures all steels are capable of forming iron nitrides in the presence of nascent nitrogen, the nitriding results are more favourable in those steels that contain one or more of the major

nitride forming alloying elements. Because aluminum is the strongest nitride former of the common alloying elements, aluminum containing steels (0.85 to 1.50% Al) yield the best nitriding results in terms of total alloy content.

### 3.3.2 Various Nitriding Processes

According to the medium used to provide the nitrogen, the nitriding process can be classified as gas nitriding, plasma nitriding, pack nitriding and salt bath nitriding.

#### 3.3.2.1 Gas Nitriding

Gas nitriding is a thermochemical surface treatment in which nitrogen is transferred from an ammonia atmosphere into the surface of steels at temperatures within the ferrite and carbide phase region. Here the workpiece is kept in an air tight box having heater around it or kept in any conventional furnace (Fig.3.26) to heat the box containing the workpiece.

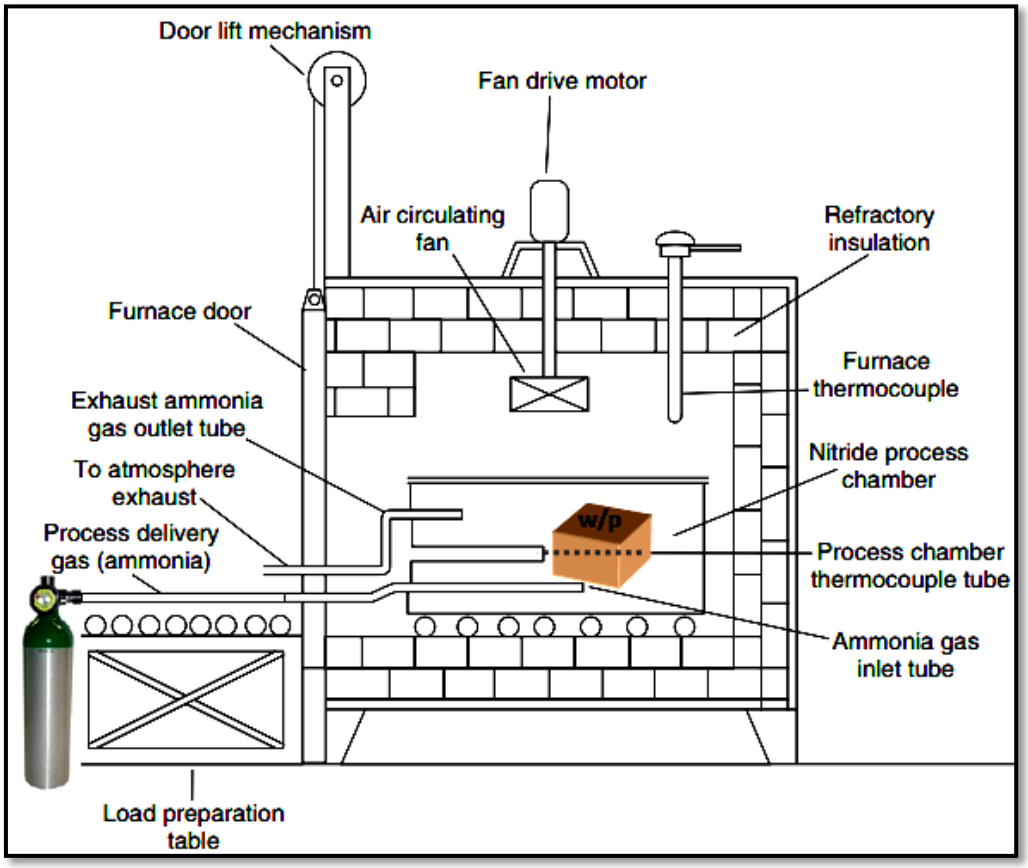



Figure 3.26: Gas nitriding process.

The nitrogen carrier gas as ammonia is continuously passed inside the box and the exhaust gas is collected from the chamber via outlet pipe. When ammonia gas gets into heated chamber, it dissociates to N and H atoms from which N is picked up by the sample surface and diffuses inside, Fig.3.27.

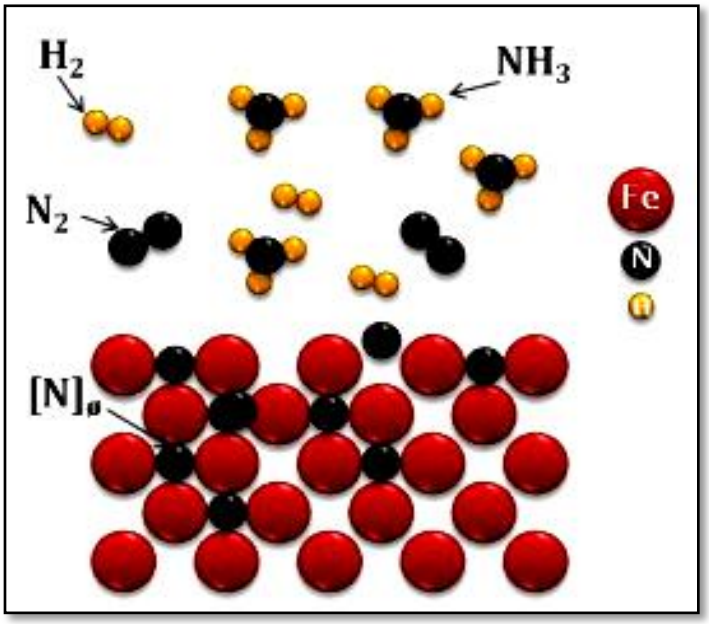



Figure 3.27: Mechanism of nascent N formation and its diffusion in iron.

After predetermined time, gas flow is stopped, power supply is cut off and the sample is collected from the chamber. In the course of nitriding, a compound layer and an underlying diffusion zone are formed near the surface of the steel. The compound layer, also known as the white layer, consists predominantly of ε- $Fe_{2-3}(C,N)$ and/or γ′-$Fe_4N$ phases (Figs.3.28 and 29), a ceramic iron-nitrocarbide layer and can greatly improve the wear and corrosion resistances.

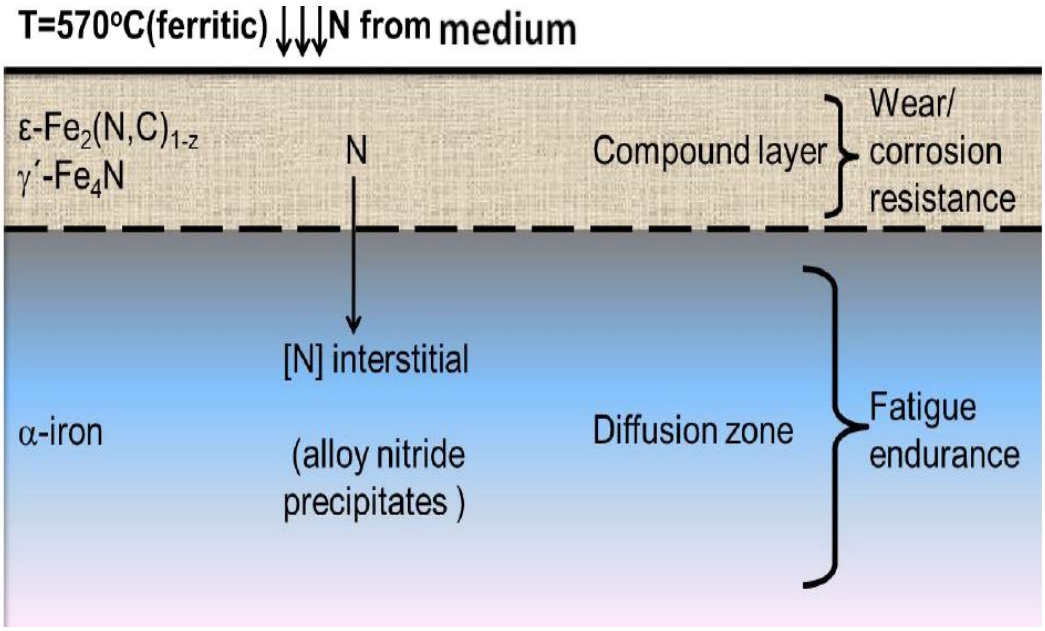



Figure 3.28: Schematic diagram showing the nitrided layer.

Figure 3.29: White nitride layer formed on low carbon steel.

The hardened diffusion zone, which is composed of interstitial solid solution of nitrogen dissolved in the ferrite lattice and nitride and/or carbonitride precipitation for the alloy steels containing the nitrides forming elements, is responsible for a considerable enhancement of the fatigue endurance. Furthermore, being a low temperature process, nitriding minimizes the distortion and deformation of the heat treated parts. Therefore, nitriding is an important surface treatment for ferritic steels. In gas nitriding, nitrogen is introduced into a steel surface from a controlled atmosphere by holding the metal at a suitable temperature in contact with a nitrogenous gas, usually ammonia, $NH_3$. The process represents one of the most efficient among the various methods of improving the surface properties of engineering components, especially the parts with complicated shapes requiring homogeneous hardening of the surface.

For the nitriding atmosphere control, the ammonia dissociation rate is traditionally adopted as the controlling parameter. It represents the percentage of ammonia dissociated into hydrogen and nitrogen and is manually measured by using a burette in the furnace exhaust gas. Since dissociation rate is not an in-situ measurement and the measurement is done manually, it introduces operator induced variability and cannot provide the accurate control on the nitriding process. A new control parameter, the nitriding potential, was introduced in the 1990‘s. The nitriding potential is defined by:

$$K_n = \frac{p_{NH_3}}{p_{H_2}^{3/2}}$$

where $P_{NH3}$ and $P_{H2}$ are the partial pressures of the ammonia and hydrogen gases respectively. By utilizing the thermal conductivity hydrogen sensor in conjunction with the two-loop controller/programmer, the nitriding potential can be calculated and controlled automatically and accurately.

### 3.3.2.2 Post Oxidation of Nitrided Surface

Nitriding or nitrocarburizing can be followed by a post oxidation step, which is performed to enhance the corrosion resistance of the material. The goal is to create a continuous layer of protective magnetite, $Fe_3O_4$, on the surface of the compound layer. The oxide layer thickness is typically in the range of a micrometer and it gives the surface a black appearance, Fig.3.30.

Figure 3.30: Various gas nitrided parts after post oxidation.

The parts can be quenched in an oxidizing medium directly after nitrocarburizing or first quenched and then oxidized. Flash oxidation is done through a few seconds exposure to the air at room temperature directly before quenching. The air exposure has to be limited to a short time since the material cannot be allowed to cool off significantly. The parts need to be quenched from above 550°C if high hardness and optimal fatigue properties are to be achieved. A notable advantage with flash oxidation is the relatively short process time. Nitrocarburizing in itself has been reported to increase the corrosion resistance of a part. However, the corrosion resistance of the compound layer can be impeded by high amounts of surface porosity. Pores increase the effective surface area of the part and consequently the corrosion rate also increases. Post oxidation fills and covers the pores in the compound layer with oxide, which is one reason for the increased corrosion resistance seen in post oxidized samples.

The second reason that post oxidation increases corrosion resistance is that it produces a passivation of the surface similar to that found in stainless steels or aluminium. The oxide film formed on the surface protects the metal from further contact with air and oxidation is slowed down because it can only continue through solid state diffusion through the oxide layer. Whether a surface will passivate or not can be influenced by the Pilling-Bedworth ratio, $R_{PB}$, which is defined as the relationship between the volumes of the unit cell of the oxide, $V_{ox}$ to the volume of the unit cell of the metal, $V_m$.

$$R_{PB} = \frac{V_{ox}}{V_m}$$

The Pilling-Bedworth is dependent on the chemical compositions of the nitride or carbonitrided surface layer as shown below.

| Interface | $R_{PB}$ |
|---|---|
| $Fe_3O_4$ - $\alpha$-Fe | 2.10 |
| $Fe_3O_4$ - $\gamma$-$Fe_4N$ | 1.80 |
| $Fe_3O_4$ - $\varepsilon$-$Fe_2N_{1-x}$ (7.3 wt% N) | 1.79 |
| $Fe_3O_4$ - $\varepsilon$-$Fe_2N_{1-x}$ (11.0 wt% N) | 1.69 |

If $R_{PB}$ is less than unity a porous and unprotective oxide is formed. Tensile stresses are developed in the oxide layer and make it crack, exposing the metal surface. If $R_{PB}$ is higher than unity, compressive residual stresses are formed in the oxide layer and passivation is possible. However, if the ratio is higher than two, the compressive stresses become too high and cause the oxide to crack and spall, destroying its protective properties. For example magnetite ($Fe_3O_4$) on ferrite has a Pilling-Bedworth ratio of 2.10 and forms an unprotective oxide layer. In nitrocarburizing the intermediate compound layer between the ferrite and the magnetite layer improves the adhesion of the oxide layer, since the Pilling-Bedworth ratio of each interface becomes lower than 2.0.

**3.3.2.3 Pack Nitriding**

Pack nitriding uses nitrogen bearing organic compounds as a source of nitrogen. The steels are packed in glass, ceramic or aluminum containers together with the nitriding compound which is often dispersed in an inert packing media. Upon heating, the organic compounds used in the process form reaction products that are relatively stable at temperatures up to 570$^{o}$C. The reaction products are decomposed at the nitriding temperature and they provide a source of nitrogen. The process time can range from 2 hours to 16 hours. This process is not so popular.

**3.3.2.4. Salt Bath or Liquid Nitriding**

Salt bath nitriding process is carried out in a molten salt bath. It can be applied to carbon steels, low-alloy steels, tool steels, stainless steels and cast iron. The case hardening medium is a nitrogen-bearing salt bath containing cyanides or cyanates. During the process, the dimensional stability of the workpiece can be preserved, thus processing of finished parts is possible. This implies that it can be used to complement engineering properties developed during carburizing and carbonitriding. This process produces toxic gases, so gradually it is getting obsolete.

**3.3.2.5. Plasma Nitriding**

Plasma nitriding uses plasma discharge technology at lower temperature to introduce nascent nitrogen on the steel surface. It is another well established surface hardening process in steel and also known as ion nitriding. Plasma is formed by high voltage electrical energy in vacuum. Nitrogen ions are then accelerated to impinge on the workpiece which is connected as a cathode. The ion bombardment heats the work piece, cleans the surface and provides the nascent nitrogen for diffusion into the steel material.

The ion or plasma nitriding process, which is based on the familiar chemistry of gas nitriding, uses a plasma discharge of reaction gases both to heat the steel surface and to supply nitrogen ions for nitriding, Fig.3.31.Various plasma heat treatment machines are currently available. In the basic arrangement common to these machines, a vacuum pump evacuates the interior of the machine and a DC voltage is applied to a workpiece using the workpiece as a cathode and the inside wall of the machine as an anode. The workpiece is subjected to nitriding and/or carburizing through application of DC voltage. When a DC voltage is applied to electrodes under reduced atmospheric pressure, glow discharge occurs across the electrodes (Fig.3.31, right).

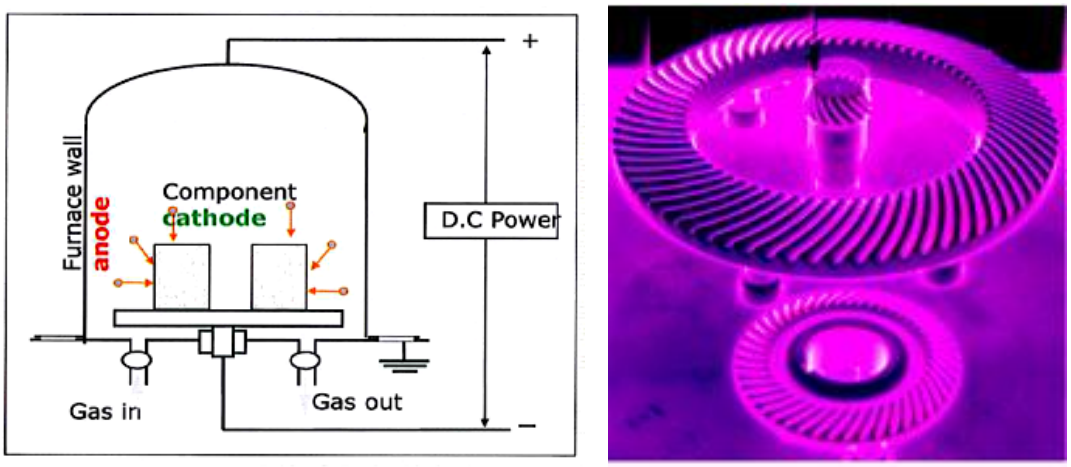



Figure 3.31: Plasma nitriding setup and glow discharge formed during the nitriding process.

Although the ion nitriding process developed by Wehnheldt and Berghaus was used successfully by German industrialists during World War II, it was not used extensively because it was considered too complex, too expensive and too unreliable to guarantee consistent and repeatable results. Not until the 1970s did the process gain industrial acceptance. The significance of the glow discharge process was that it did not rely on the decomposition or cracking of a gas to liberate nascent nitrogen on the steel surface. The process was based on the ionization of a single molecular gas, which is nitrogen and the liberation of nitrogen ions. The process offered a shorter cycle time due to the steel surface preparation and the gas ionization. During glow discharge, electrons are released from the cathode toward the anode. These electrons collide with molecules introduced into the machine, converting the gas molecules into ions. The resulting ions are accelerated toward the cathode (that is, the workpiece), penetrating into the workpiece surface when they collide with the surface. One outstanding advantage of plasma heat treatment is the lower environmental impact it poses compared with heat treatment with a controlled atmosphere furnace. For example, nitriding with a controlled atmosphere furnace often uses ammonia gas. In contrast, using a plasma nitriding technique, a steel material can be nitrided with nitrogen and hydrogen. Also, with plasma nitriding, the intended workpiece alone is heated without heating the entire interior of the furnace; a practice necessary for a controlled atmosphere furnace. Following Fig.3.32 shows schematics of typical plasma heat treatment equipment configurations. With cold wall or hot wall configurations where a bias voltage is

applied to a workpiece, a clean surface is exposed on the workpiece through sputtering where ions collide with the workpiece. Consequently, the surface of a material is nitrided in a short time even if the material type needs a longer time for nitriding with a gas nitriding or vacuum nitriding process. However, conventional plasma heat treatment techniques have disadvantages such as poor surface smoothness resulting from sputtering. To address this problem, a unique configuration known as the "active screen" method has been developed, wherein a bias voltage is not applied to the workpiece.

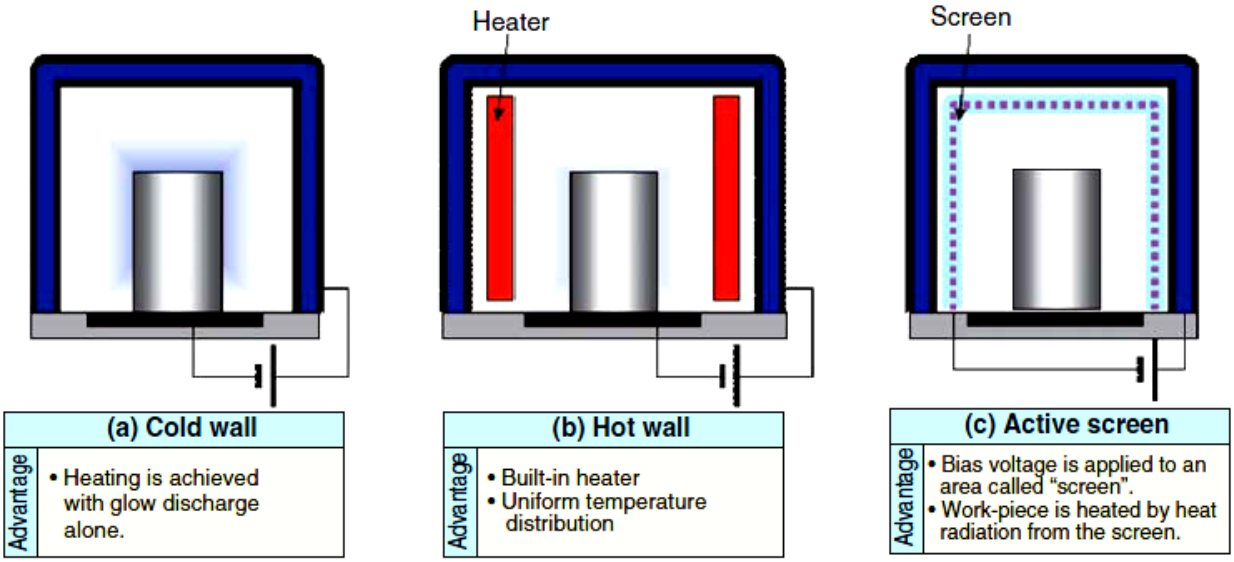



Figure 3.32: Various heating configuration in plasma nitriding process.

### 3.4 Selective Hardening Methods

For selective surface hardening, the chemical composition is not modified anymore. As a result, the steel component must have sufficient carbon or alloying elements that can provide them optimum hardenability. Here the surface heating rate and time in synchronized in such a way that up to the required hardened depth is only transformed to austenite only. So, after heating, when the component is quenched the depth containing austenite is transformed to martensite keeping the core unchanged. There are several options for selective surface hardening such as flame hardening, induction hardening, laser hardening, electron beam hardening, ion implantation and so on.

#### 3.4.1 Flame Hardening

Flame hardening is a selective surface hardening treatment where the outside of the component is uniformly heated by direct application of a flame, Fig.3.33. Special burners combining a fuel gas (typically acetylene) and oxygen are used to generate the flame. Temperature is monitored optically comparing the color of the heated steel to a color/temperature chart as well as using infra red temperature sensors. When the heating transforms the microstructure of the component to austenite up to a predetermined depth, the part is then rapidly cooled to get martensitic structures.

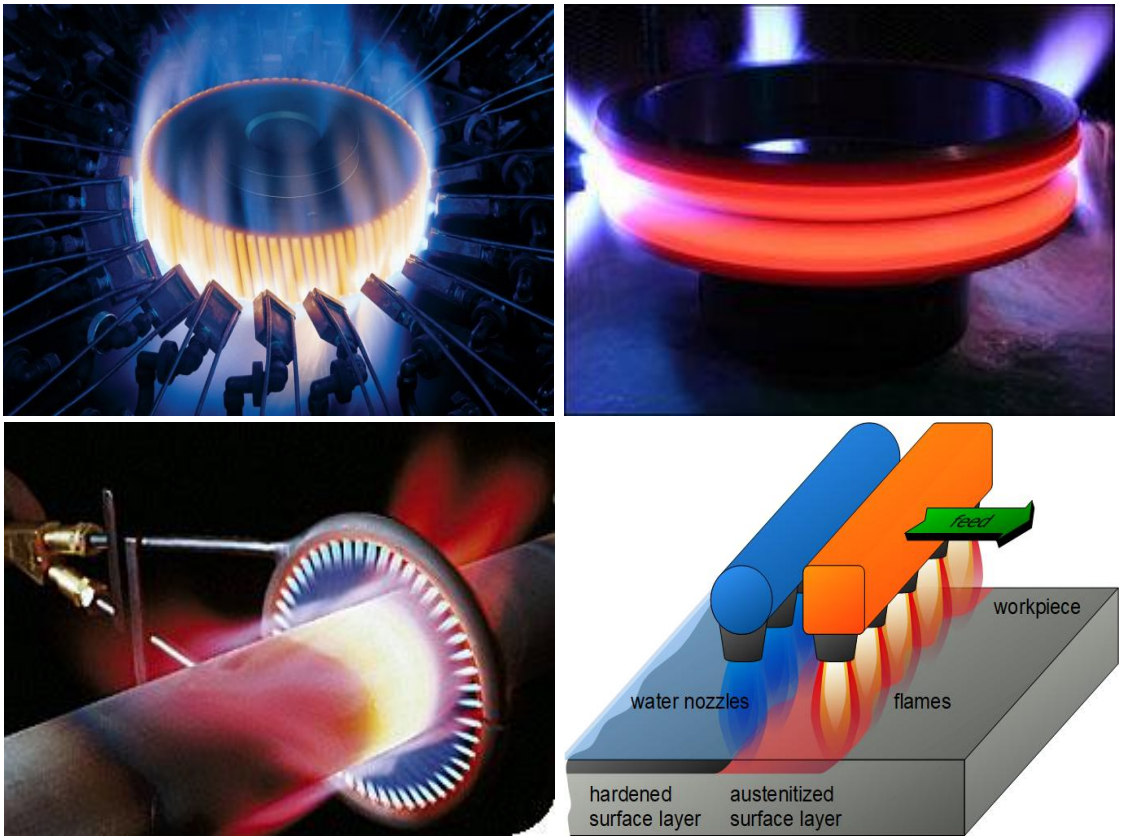


Figure 3.33: Preferential surface heating by oxy-acetylene flame.

The component is then tempered to the appropriate hardness and microstructure. This results in a highly wear resistant surface, as well as increased bending fatigue strength, while leaving a tough core which can absorb shock and loading. Gears, wheels, rolls and other cylindrical parts are spin flame hardened. They are placed on a motorized table and spun while a flame impinges on the outer diameter of the wheel. For flame hardening to be effective, the component being hardened must have a carbon content of greater than 0.3% carbon.

Quenching is performed in water, polymer solutions, oil or compressed air. In flame hardening much greater hardening depths up to 40mm can be realized by flame hardening. The depth which is to be hardened can be adjusted by changing the feed rate of the hardening burner. Another advantage of flame hardening is the possibility to harden even very large and voluminous work pieces. Furthermore, the flame hardening is suitable for many different applications, even small lot sizes or single items. The hardening burner and the quench are designed for the requirements of the work piece. The hardening burner can be used with fuel gases such as Acetylene, natural gas, Propane and Butane together with Oxygen. The required equipment for flame hardening includes standard flashback arrestors, hoses and pressure regulators.

### 3.4.2 Induction Hardening

Induction heating is an extremely versatile heating method that can perform uniform surface hardening, localized surface hardening, through hardening and tempering of hardened pieces. Heating is accomplished by placing a steel ferrous part in the magnetic field generated by high frequency alternating current passing through an inductor, (a water cooled copper coil), Fig.3.34.

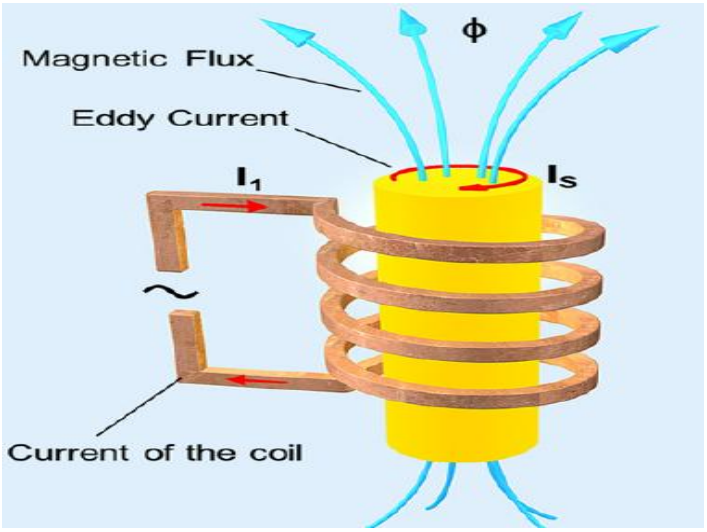



Figure 3.34: Preferential surface heating by induction heating process.

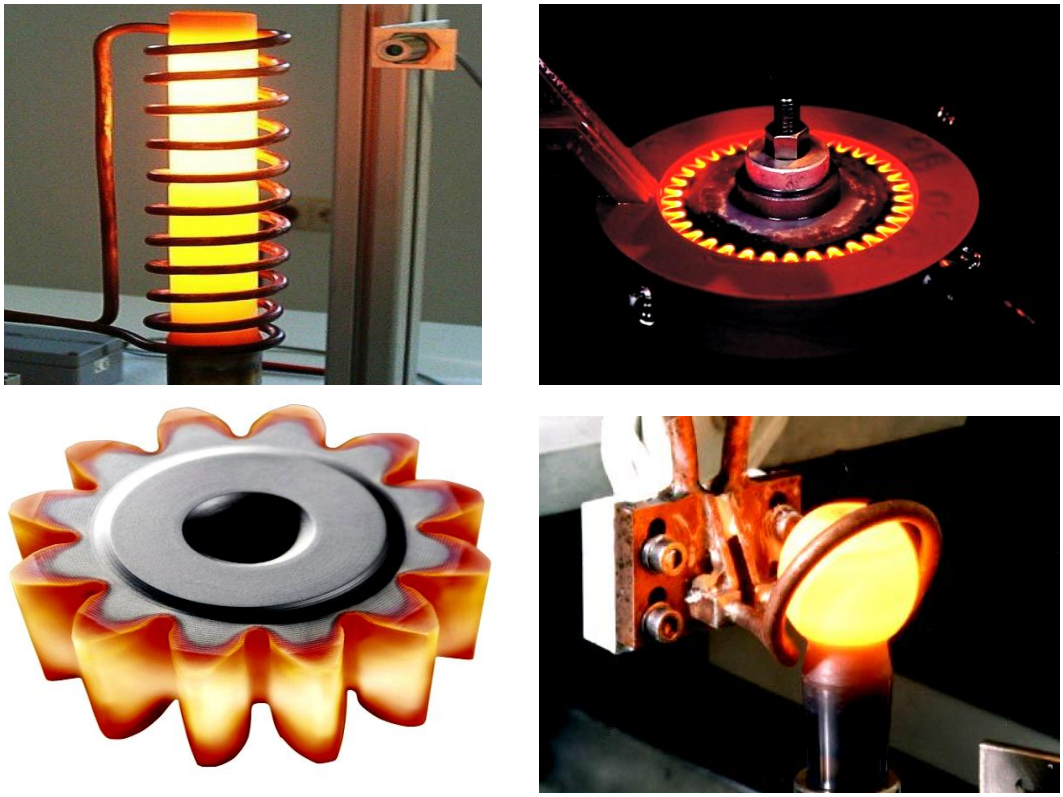


Figure 3.35: Some parts heated by induction heating process.

The depth of heating produced by induction is related to the frequency of the alternating current, power input, time, part coupling and quench delay. The higher the frequency, the thinner or more shallow the heating. Therefore, deeper case depths and even through hardening are produced by using lower frequencies. The electrical considerations involve the phenomena of hysteresis and eddy currents. Because secondary and radiant heats are eliminated, the process is suited for in-line production. Some of the benefits of induction hardening are faster process, energy efficiency, less distortion and small footprints. Care must be exercised when holes, slots, or other special geometric features must be induction hardened, which can concentrate eddy currents and result in overheating and cracking without special coil and part designs. Surface hardening by induction heating processes of some components are shown below in Fig.3.35.

### 3.4.2.1 Design in Induction Hardening

In selective hardening, the depth of hardened layer depends up to which the materials have been transformed to austenite. In general, the depth is defined as the point where induced electric current decreases to about 37% compared to the current at the surface and normally expressed as δ, Fig.3.36. The value δ is calculated as follows:

$$\delta = 5.03x\sqrt{\frac{\rho}{\mu f}}(cm)$$

Where, δ = Penetration depth (cm), μ = Specific permeability (magnetic materials: μ>1, non-magnetic: μ = 1), f = frequency (Hz), ρ = specific resistance (μ Ω.cm).

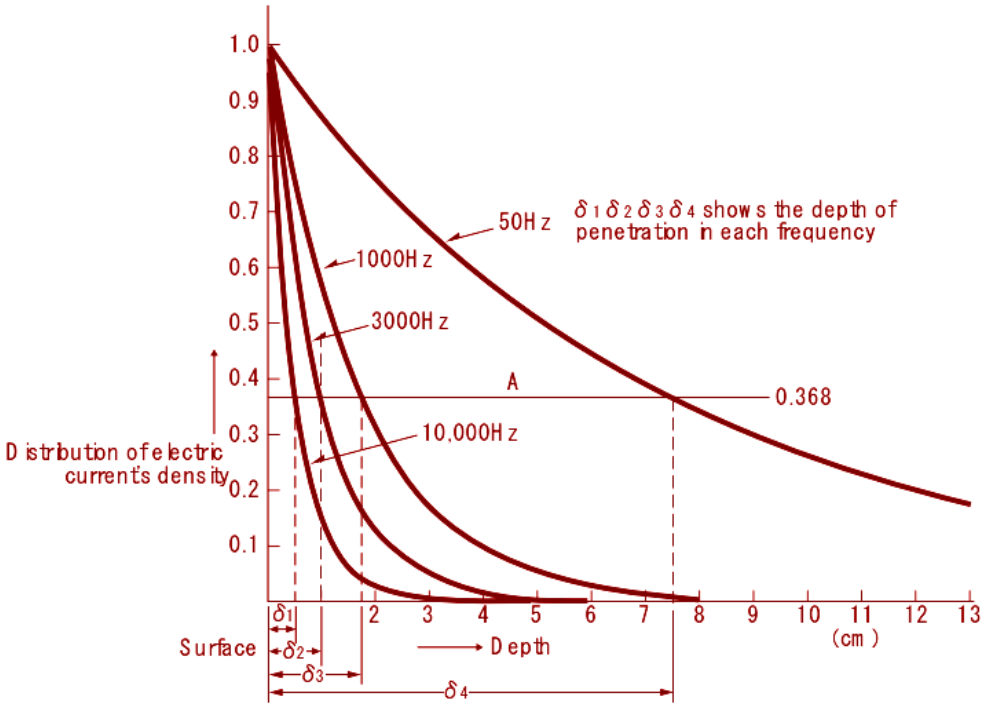



Figure 3.36: Effects of frequency on the heat penetration depth.

The formula shows that as the frequency is higher, δ will be lower and heating will be concentration at the surface if compared for identical materials. The required electric power P is supplied from the induction heater through inductor. The heating mass is the product of surface hardening are, hardening layer depth and specific gravity. However, accurate calculation of heat losses such as heat conduction loss and so on is very difficult. So, it is better to calculate based on experience and experienced data.

### 3.4.2.2 Choice of Frequency and Electric Power

For effective induction hardening, the suitable frequency of the induction power generator must be chosen. The quality of hardened layer obtained by induction process depends upon frequency, electric power density, heating temperature, cooling speed, pre-processed condition (cold, warm or hot worked) and so on. Therefore, frequency and power density must be chosen according to the size of work piece and hardening specification, e.g. depth of hardened layer, hardness level, microstructures, etc. So, the capacity of the induction generator to be used should be decided according to the mass, heating temperature and heating time of the material to be hardened. The calculation of heating power except heat losses in inductor and coupling between inductor and the work piece is given below:

P (required power) = $P_1 + P_2 + P_3 + P_4$
$P_1$ = Absorbed power by heating material
$P_2$ = Radiation heat loss
$P_3$ = Convection heat loss
$P_4$ = Conduction heat loss

$P_1$, $P_2$, $P_3$ and $P_4$ are calculated as follows:

$P_1 = 4.186 \times M \times C \times \Delta T$ (kW/sec), M = Mass in kg, C = Specific heat, ΔT = Surface temperature $^oC$

$$P_2 = 5.7e\{(\frac{273+t_2}{1000})^4 - (\frac{273+t_1}{1000})^4\}\ W/cm^2$$

$t_1$ = Normal temperature, $t_2$ = Heating temperature, e = Radiation ratio (for steel: 0.8)

$$P_3 = 159\Delta T(\mu W/cm^2$$

ΔT = Surface temperature rise $^oC$, μW = Micro watt

$$P_4 = 3.72\Delta T\sqrt{\frac{KCS}{t}}(\frac{W}{cm^2})$$

K = Heat conductivity, C = Average specific heat, t = Heating time, sec

**Problem 3.3:** How much power capacity in kW is required for an induction heater to make hardened a round steel bar work piece of diameter 25in, 50mm in length to obtain 1.5mm hardened depth from the surface in the circumference along 50mm length by heating 2 seconds?

**Solution:** Weight of the w/p = $\pi \times r^2 \times h \times$specific gravity = 0.0429kg
Net absorbing power P = 4.186×Weight of heating part×Average sp heat×Heating temperature = 4.186×0.0429×0.15×900 = 24.24 kW/s

It is difficult for accurate calculation of heat loss by radiation, convection, conduction, circuit loss, coupling loss, etc. So, experience is very important. As per expert in this field, total heat supply is considered to be three times of the net absorbed power.

So, the total output power of the generator = 24.24×3 = 72.72 kW/s

The heating temperature should be raised by 2 seconds. So, the power capacity of the induction heater will be 72.72/2 = 36.36 kW.

$$\delta = \sqrt{\frac{\rho}{\mu f}} cm$$

Now, the frequency $f$ = Frequency (Hz), μ = Specific permeability (1 for iron), ρ = Specific resistance (μΩcm) = 115 at 900°C.

The optimum frequency of the induction heater $f$ will be ~5kHz. The required frequency of the induction heater can also be guessed from the following curves presented in Fig.3.37.

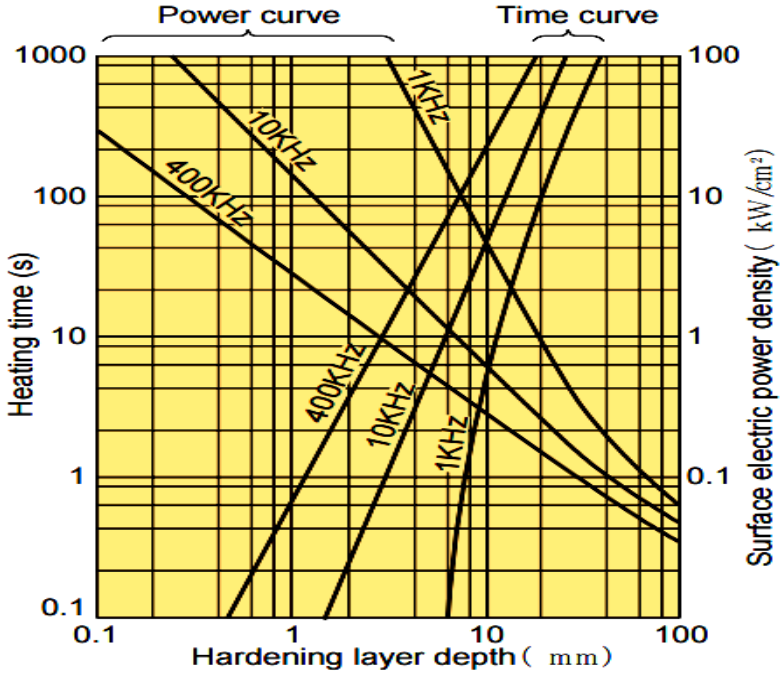



Figure 3.37: Relation among hardened depth of steel, frequency, power density and heating time.

### 3.4.3 Surface Hardening by Laser

Laser hardening belongs among the core technologies of heat treatment. Here, laser beam is used for heat treatment of the targeted area. The high energy density of the laser enables a very rapid heating of the area to be hardened above the austenitic temperature. In this technique, “self quenching“ phenomenon applies after removing the heat source from the interaction zone without any quenching media, i.e. laser heating and hardening actions run simultenously, Fig.3.38.

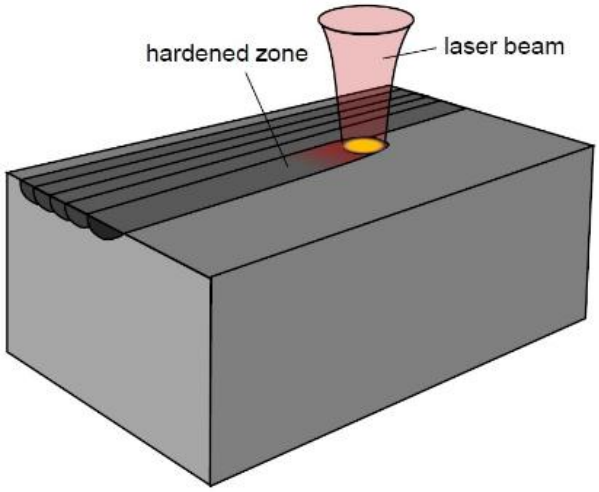



Figure 3.38: Laser heating for surface hardening.

The surface hardened zone of a component is shown below in Fig.3.39. From the hardened surface towards the core, there is a zone, where all phases do not transform to austenite. As a result, that area is partially hardened called transition zone.

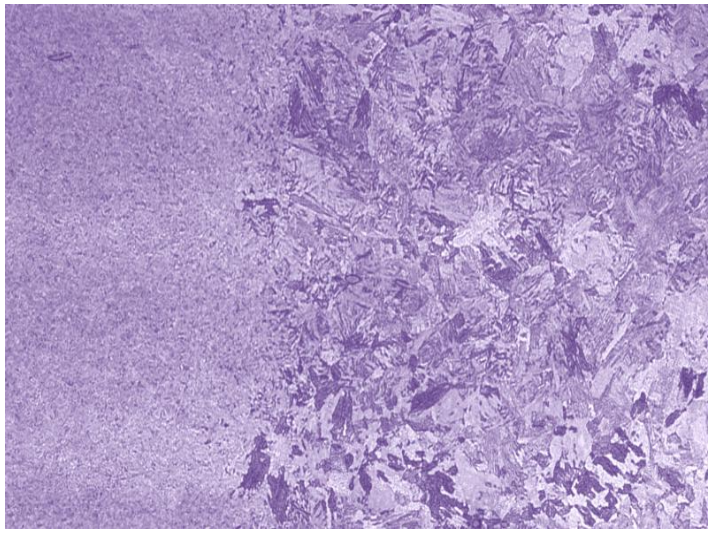


Figure 3.39: Modification of surface layer after laser hardening.

Thermal energy absorbed by surface layer is quickly distributed to the entire workpiece. This heat diffusion results in a very rapid temperature drop in the hardened area. In laser beam heating scale is an order of magnitude shorter. The power of the beam and the diameter of the focused laser beam can be combined to give one laser parameter, the power density. The second and other parameter of laser treatment is the rate at which the power density is moved across the surface of the object. In surface hardening using laser radiation, the material (carbonic steel) is heated above the austenization temperature for a short time. Through rapid cooling the steel reaches the martensitic material structure. Heat deposition is realized through the absorption of laser radiation at the surface of the material, whereas cooling occurs conductively within the remaining material. The thermal gradient is mainly defined by the laser spot geometry and the feed rate. In laser processing, laser light is directed to the workpiece resulting in absorption and reflection of light. Absorption by metals is highly dependent on the wavelength of light, material type, angle of incidence and surface condition. In general, the shorter the wavelength, the better light is absorbed. Lasers used for heat treating have wavelengths that fall between 800 and 10,600 nm. The time period, or exposure period, generally is less than one second. The shape of the hardened zone varies with the shape of the spot and the energy distribution across the spot produced by the beam. There are many methods that can be used to modify the beam, but the most common spot shapes are circular and square. A circular spot produces a hemispherical, while a square spot produces a relatively flat base and even hardened zone.

It has been mentioned that the heat input rate of a laser beam is very high. It can be further increased by controlling the wavelength of the beam. The shorter the wave length, higher the energy input. Other parameters to control the energy input rate are geometry of laser sot and materials. By controlling all parameters in convenient way, one can use the laser beam for various purposes for materials study as shown in Fig.3.40.

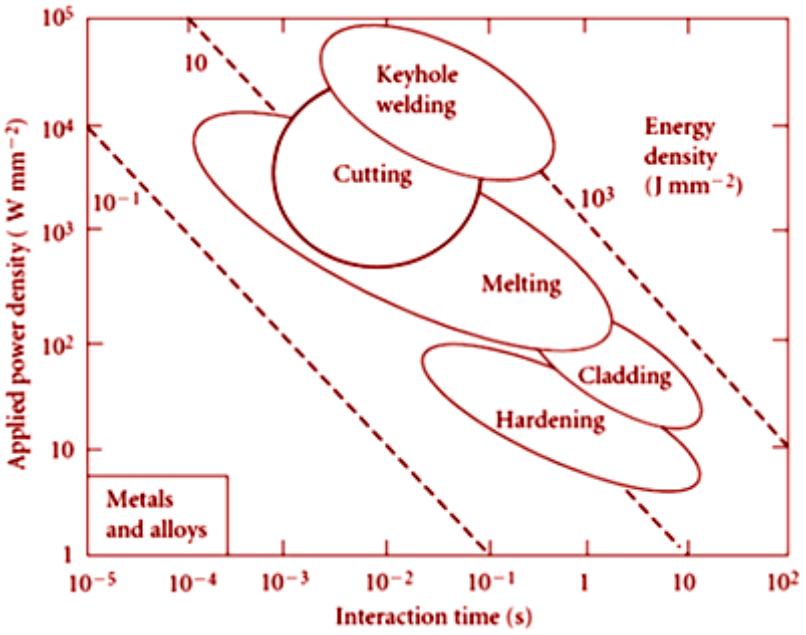


Figure 3.40: Energy absorption of capacity of various materials.

When compared with conventional hardening methods such as oven case, flame or induction hardening, laser hardening is marked by a range of advantages such as the spatially and temporally limited energy deposition, contactless energy deposition, highly defined energy deposition and hardness, self cooling through thermal conduction, stable process, crystalline hardening structure, controllable process, contactless temperature measurement using, pyrometry. All conventional hardening methods require quenching with water, oil or salt bath. When using oven or case hardening, the whole component is heated, resulting in very long heating times what is often combined with through hardening of the entire part. Because the laser light beam is finite in size, the process is ideally suited to perform specific localized area treatment. Controlled heat input, self quenching of parts, no need for special atmospheres and process cleanliness are some advantages of laser hardening technology. In addition, these attributes often translate into reduced costs because of lower distortion and lower use of consumables. Other advantages are very localized and thin surface layer hardening or repairing by laser technique, Fig.3.41.

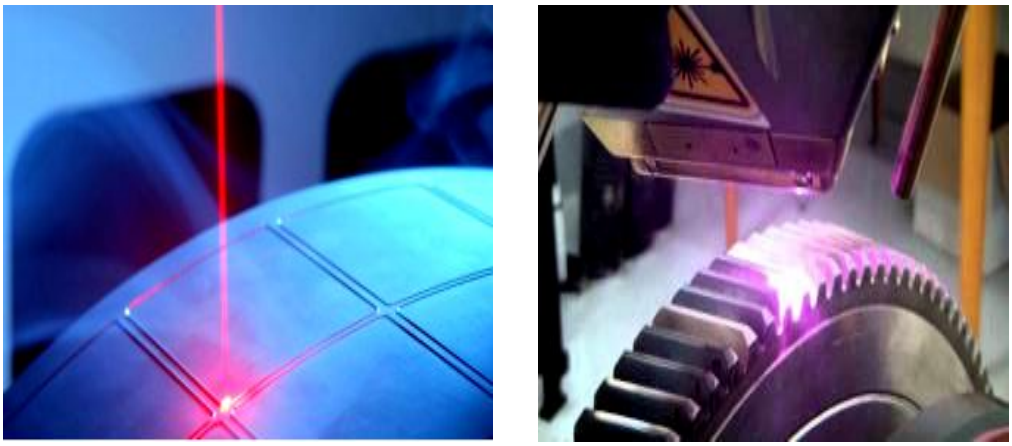


Figure 3.41: Lacalized surface heating and hardening/repairing by laser process.

### 3.4.3.1 Design of Laser Hardening

Laser transformation hardening (LTH) is a very quick and localized heat treatment process involving only heating, with relatively low values of energy consumption. This can be used for a wise version of purposes. Here the heating rate is so high that slight mismanagement in time might cause melting of the materials. In LTH, total heating period is in the range of second, Fig.3.40.

In this technique, the calculation of energy density is possible by using following equation:

$$\boldsymbol{Energy\ Density\ (ED)\ = \frac{P}{D_{SS}V}}$$

Here P is the laser beam power and V is the travel speed of the beam. The laser spot size $D_{SS}$ is calculated using equation:

$$\textbf{\textit{Laser Beam Spot Diameter}}(D_{SS}) = \frac{4M^2\lambda f}{\pi D_{BS}}$$

Here λ is the wave length (mm); *f* is the lens focal length (mm); $D_{BS}$ is input beam diameter at the lens (mm); M is the beam mode parameter, which expresses how quickly a given beam diverges while propagating. The power density (PD) is directly related to the laser power (P) and the beam coverage area (A) in the material. It can be calculated from the equation PD = P/A, where $A = \pi r^2$, r is the radius of the spot size. The Laser beam may be convergent or divergent. In the case of convergent beam, the relation between $D_{BS}$ and $D_{SS}$ is given below.

$$D_{BS} = \frac{2\lambda f}{D_{SS}}$$

After Laser heating, the steel surface is self quenched that results martensitic microstructure. In the following Fig.3.42 the martensitic structures that are formed by LTH in ferrite-pearlitic structures of a low alloy steel is shown.

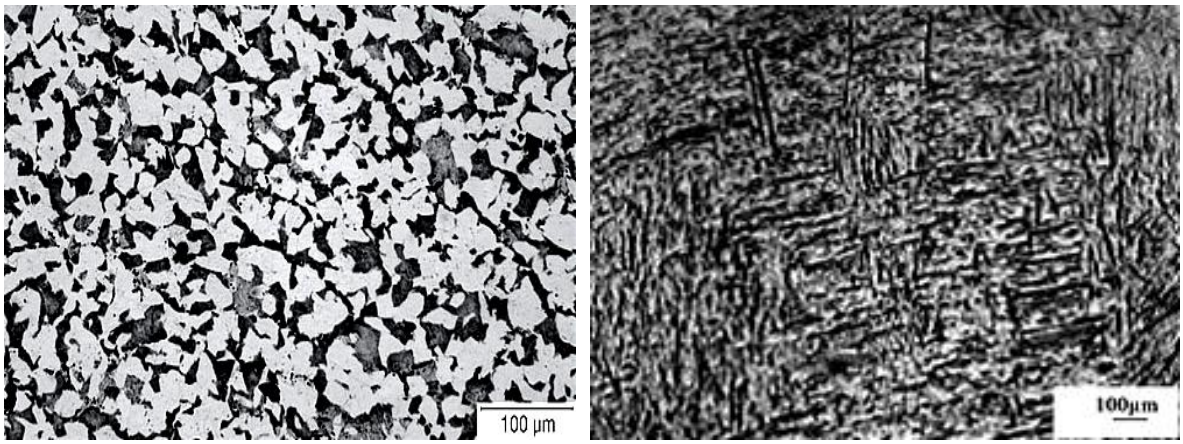



Figure 3.42: Microstructures of low alloy steel before (left) and after (right) Laser surface modification.

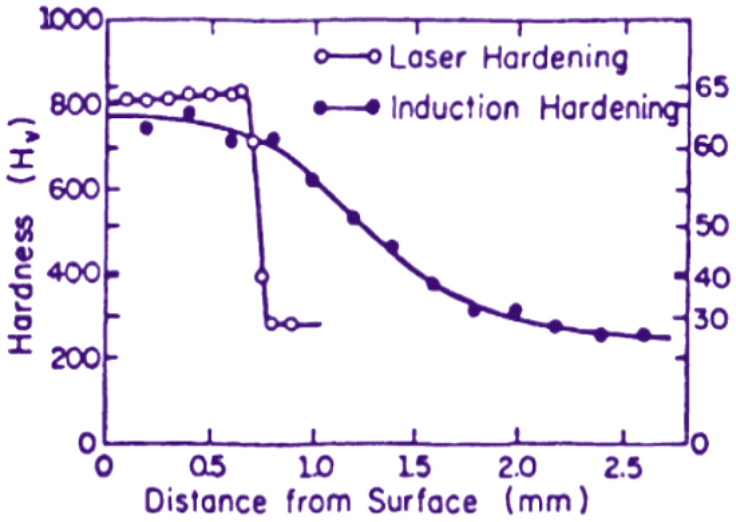


Figure 3.43: Hardness distribution comparison between laser hardening and induction hardening

As the heating duration is short, the hardened zone presents less distortion and surface oxidation than that obtained in flame or induction hardening. Figure 3.43 shows the distribution of hardness values obtained after laser hardening as compared to induction hardening. The higher values for laser hardening near the surface are due to the much finer and highly restrained martensites in the laser-hardened microstructures compared to the other case. Moreover, surface modification is very localized because of very quick heating system. In induction hardening heating rate is also fast, but not as fast as in the case of laser process. As a result, induction hardening results a large transition zone. LTH process is suitable for selective surface treatments and is primarily used in steels with sufficient hardenability for improvement of wear resistance and fatigue strength.

**Problem 3.4**: A Laser heating system of 1500 W with convergent lens is being used for one second in transformation hardening of an alloy steel surface. If the focal length, spot size and wave length of the laser beam are, respective, 300mm, 1.5mm and 10μm, calculate size the Laser beam and M factor value. Consider beam scan rate 400mm/min. Give your comment for this LTH.

**Solution**: $D_{BS}$ = 6mm, M = 1.237, Yes, LTH is possible by this Laser system.

### 3.4.4 Electron Beam Surface Hardening

Since the forties of last century, tests have been made to use and weld metals by means of accelerated electrons. Heat is not put in conventionally through heat conduction and convention, but through transformation of kinematic energy of electrons into heat. At the end of the fifties of last century it became possible to join thicker plates by butt welding. This had been the starting point of industrial utilization. Mainly nuclear engineering, aviation and aerospace industries are more and more profiting from this new technology.

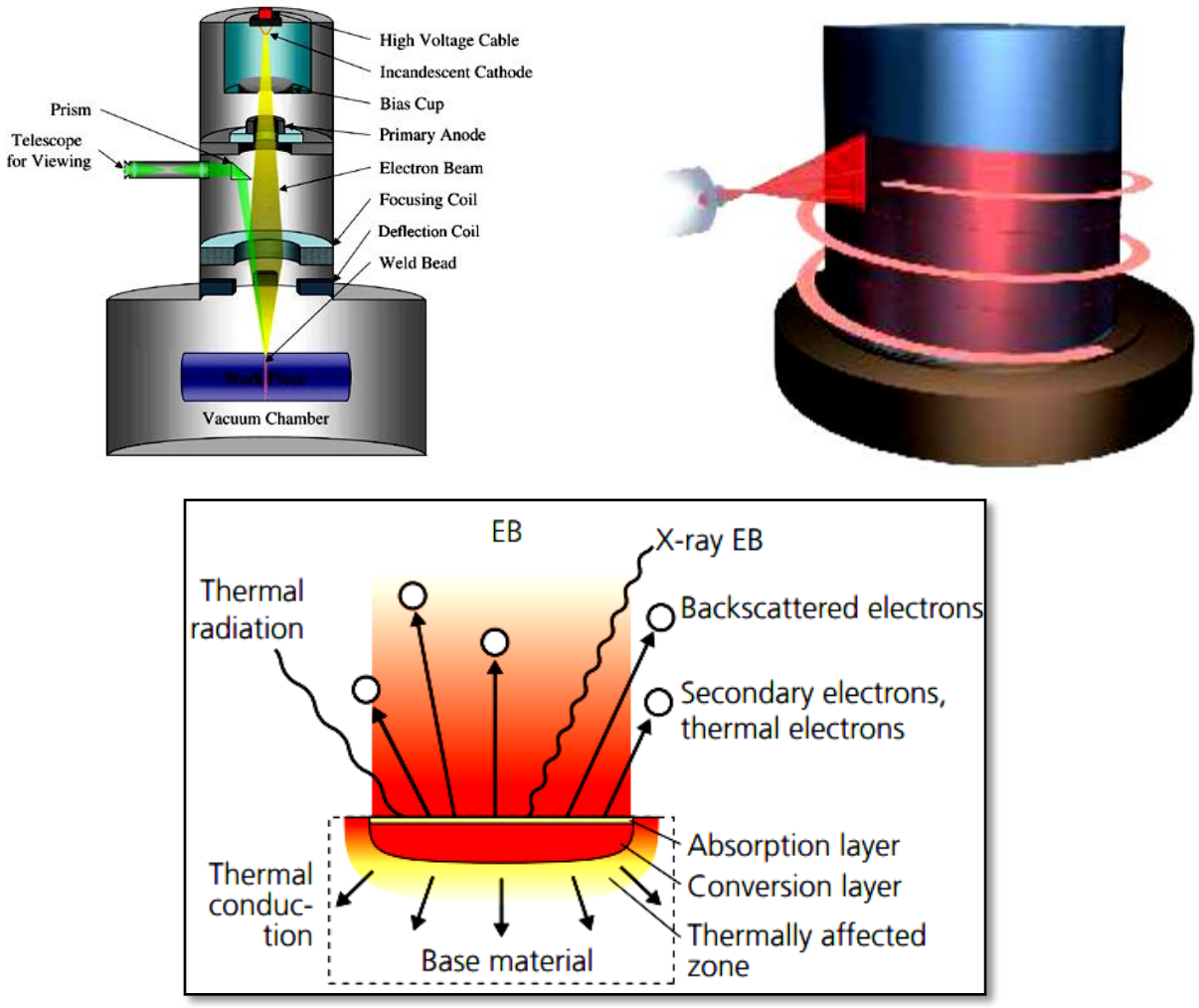



Figure 3.44: Electron beam heating setup and surface hardening mechanisms.

Electron beam technology is a promising technology especially under the aspect of continuously rising raw material prices. In this technique relatively wide beam of electrons is bombarded over the surface of the product, Fig.3.44 and the sample surface gets heated above the austenitizing temperature and after specified time, electron bombardment is stopped and the surface of the product gets self quenched.

Using intensive pulsed electron beams, energy can be deposited into surface layers of materials very efficiently and fast. There is complex interaction between applied electron beam and the material surface to be treated by which X-ray, backscattered electron and secondary electrons are produced. Because of intensive heat generation capacity, material surfaces are melted with a single pulse to a depth of up to 100µm depending on the specific energy input (5-60 J/cm²). After termination of the pulse (some 10µs) the melt layer cools by heat conduction with cooling rates of 106-109 K/s. Thereby, microcrystalline, nanocrystalline or even amorphous structures in the modified surface layer are formed that show improved hardness, corrosion resistance and wear resistance. Currently, the most important application is surface alloying of metals with different

materials. The alloying of aluminum into steel surfaces for improved corrosion resistance is in the focus of the application related work. High speed cameras in streak and framing mode allow the in situ observation of the surface melting process. Applying ultra short time spectroscopy, the state and properties of evapourated material close to the surface can be investigated. The results of in-situ analyses are combined together with simulations to understand and describe the physical processes during remelting and cooling. Pulsed electron beams with large diameter and sufficient beam energy can be created using high voltage generators and vacuum diodes. As electron source a multipoint explosive emission cathode consisting of several carbon fiber bundles is used.

# Chapter Four

## Heat Treatment of Cast Iron

### 4.1 Introduction

Cast irons are also ferrous alloys, where the carbon content is higher than 2.0%. Moreover, compared to steels, the proportion of impurity and trace elements in cast irons are also somewhat higher. Another important feature of cast iron groups is that they are shaped directly through casting process because of their low melting temperature, higher fluidity in the molten conditions and less defects associated with the cast products.

Pure, carbon-free iron is practically never used, because in the cast form it is soft and weak. As carbon content increases, so does hardness and strength. The beneficial effect of carbon, although creating production problems, is advantageous to about 0.9% carbon. These alloys are called steel. Additional problems are encountered with carbon contents to about 2.0% and these "semisteels" are seldom used. Cast iron usually contains more than 2.0%C. There are several varieties of cast irons among which the followings are very widely used.

a) White cast iron, b) gray cast iron, c) malleable cast iron, d) nodular or spheroidal or ductile cast iron, etc.

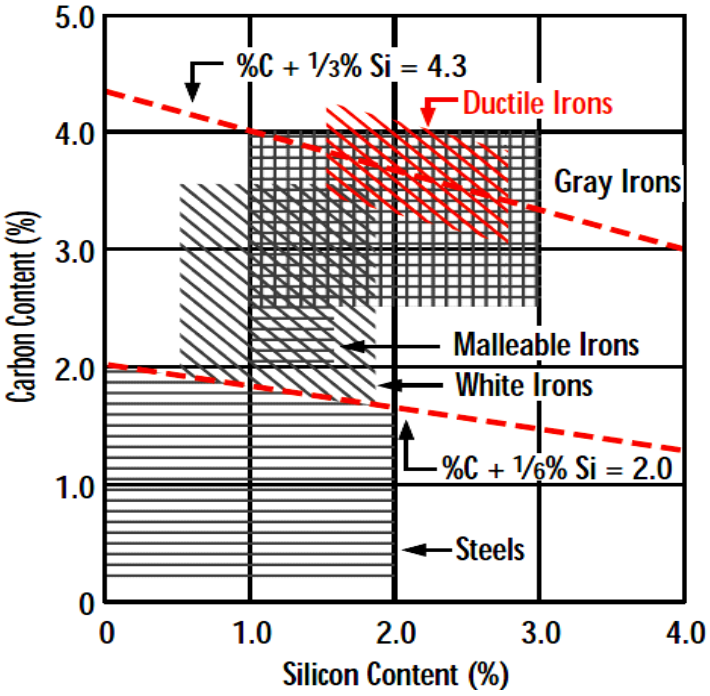



Figure 4.1: Carbon and silicon in various cast irons

White cast iron, containing 2 to about 3.3% carbon, can be used for highly abrasive service, but the application is limited due to the brittle nature of the alloy. It is a true cast iron, but most of the contained carbon is present as iron carbide $Fe_3C$, a hard and brittle compound. In commercial cast irons, carbon content is within 4.5%. In cast irons, silicon content plays the vital role to control the carbon morphology of their microstructures and thus the varieties. Malleable cast iron is the heat treated product of white cast iron. So, indeed, malleable iron must solidify as white iron. Malleable cast iron the carbon contents of white and malleable irons overlap, Fig.4.1. For the production of white cast iron very high cooling rate is required. However, with the increase in section thickness the cooling rate naturally decreases. As malleable cast iron is the heat treated products of white cast iron, so its production is limited to relatively thin castings only.

In gray and ductile irons, carbon in excess of its solubility in solid iron is present as finely dispersed graphite shapes, rather than as $Fe_3C$ (cementite, iron carbide). In gray cast irons the graphite flakes act as stress raisers and under stress help crack propagation, Fig.4.2. As a result, gray cast irons are weak, with ultimate tensile strength is the order of 20,000 to 50,000psi (150 to 350MPa) and with practically no elongation. The size of graphite flakes varies with production conditions and also with casting thickness. Normally, flake lengths are from 0.1 to 1.0 mm. cast iron with spheroidal graphite (i.e. ductile iron) became an industrial reality in 1948. A suitable treatment of the molten iron causes the graphite to precipitate as spheroids, rather than flakes, Fig.4.2. The nearly spherical shape of the graphite removes the "crack" effect and, in fact, the graphite spheroids act as "crack arresters" (Fig.4.2).

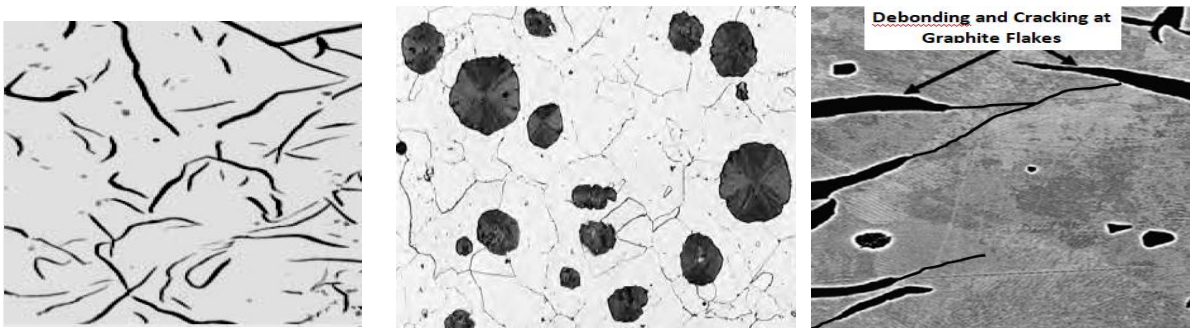



Figure 4.2: Cracking modes in gray (left) and nodular (right) irons.

In the case of steel, a wide range of heat treatment options are available. However, for cast irons, the heat treatment options are somewhat limited. Before discussing the heat treatment processes of cast irons, the effects of some important alloying elements on various properties of cast iron have been discussed below. Here it is to be noted that the effects of alloying elements in cast irons are somewhat different compared to that in steels.

**I) Silicon**: Silicon is a graphitizer. It enhances the formation of free carbon along with ferrite. So, it provides the ferritic matrix with the pearlitic one. Silicon enhances the performance of ductile

iron at elevated temperature by stabilizing the ferritic matrix and forming the silicon reach surface layer, which inhibits the oxidation. The potentially objectionable influences of increasing silicon content are:

i) Reduced impact energy.
ii) Increased impact transition temperature.
iii) Decreased thermal conductivity.

**II) Manganese and Sulphur:** These two elements have some mutual effects. Sulphur remains in the melt either in the form of FeS (iron sulphide) or MnS (manganese sulphide). Sulphur in the form of FeS tends to promote cementite. In presence of Mn, however MnS or complex manganese-iron-sulphides forms which begin to precipitate early and continue to do so during entire freezing process and are, therefore, usually randomly distributed. The effect of Mn alone is to promote resistance to graphitisation. Thus, Mn above that necessary to react with the sulphur will help in retaining the pearlitic microstructure. In view of attaining desired microstructure, the sulphur-manganese relationship is expressed as below:

a) % S x 1.7 = % Mn; Chemically equivalent S and Mn percentage to form MnS considering no effect from iron.
b) % S x 1.7 + 0.15 = Mn; the Mn percentage which will promote a maximum of ferrite and a minimum of pearlite.
c) % S x 3 + 0.35 = Mn; the manganese percentage which will develop a pearlitic microstructure.

**II) Phosphorus**: It practically does not influence the graphite-cementite ratio. It often occurs as steadite, a eutectic of iron and iron phosphide of low melting point. In the production of sound castings of heavy sections, phosphorus should be reduced to about 0.3% in order to avoid shrinkage porosity.

**III) Copper**: It is a strong pearlite promoter. It increases the proof stress with also the tensile strength and hardness with no embrittlement in matrix. So, in the pearlitic grade of the cast iron the copper is kept between 0.4-0.8%.

**IV) Nickel**: As it helps in increasing the UTS without affecting the impact values, it can be added in the range of 0.5-2.0. It strengthens ferrite without no or a very little decrease in ductility. But there is the danger of embrittlement with the large additions; in excess of 2%. Due to the high cost it is generally present as traces in the matrix.

**V) Molybdenum**: It is a mild pearlite promoter and forms intercellular carbides, especially in heavy sections. Mo increases proof **Phosphorus**: Phosphorus in cast irons is kept intentionally very low, because it causes cold shortness and reduction in required properties of ductile iron. But the addition of S is done for better machinability, which is kept around 0.009 to the maximum value of 0.015%. As the larger additions of sulphur may cause the hot (red) shortness.

stress and hardness. It also improves elevated temperature properties. Mo is a very strong carbide former and coarsening of carbide particles results decrease in tensile strength.

**VI) Chromium**: It prevents the corrosion by forming the layer of chromium oxide on the surface and stops the further exposition of the surface to the atmosphere. But as it is a strong carbide former, so not good to be added in any cast iron where carbide free structure s required.

### 4.2. Gray Cast Iron

Gray Irons are the groups of cast irons that form flaky graphite during solidification (Fig.4.3), in contrast to the spheroidal graphite morphology of ductile irons. The flake graphite in gray irons is dispersed in a matrix with a microstructure that is determined by composition and heat treatment. The usual microstructure of gray iron is a matrix of pearlite with the graphite flakes dispersed throughout the matrix. In terms of composition, gray irons usually contain 2.5 to 4% **C**, 1 to 3% **Si** and additions of manganese, depending on the desired microstructure (as low as 0.1% **Mn** in ferritic gray irons and as high as 1.2% in pearlitic). Other alloying elements include nickel, copper, molybdenum and chromium.

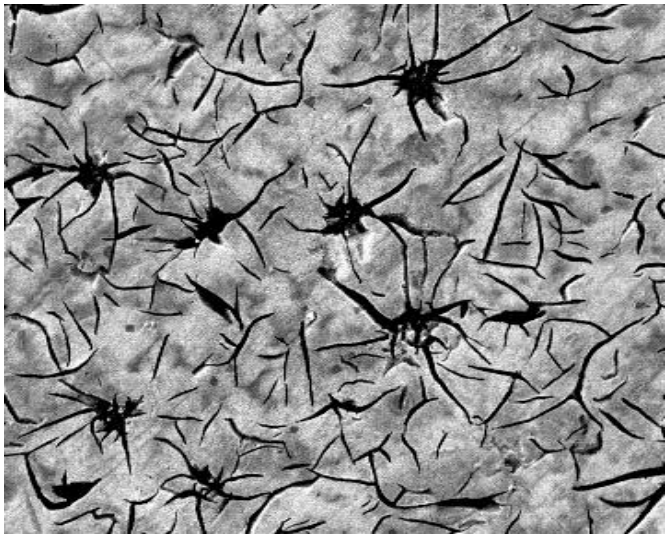


Figure 4.3: Microstructures of gray cast irons

### 4.2.1 Cast Iron Hardening Basics

In any discussion of the heat treatment of cast irons it is important to understand the concept of carbon equivalent (CE). The CE establishes the relationship between the effects of alloying elements in an iron and the amount of carbon that would be required to provide a similar heat treatment effect. Several expressions have been developed. One presented below is most widely used.

$$CE = \%C + 0.3(\%Si) + 0.33(\%P) - 0.027(\%Mn) + 0.4(\%S)$$

In general, lower the carbon equivalent the better will be the hardenability of the cast irons. The heat treatment of gray irons can considerably alter the matrix microstructure with little or no effect on the size and shape of the graphite achieved during casting. The matrix microstructures resulting from heat treatment can vary from ferrite pearlite to tempered martensite. However, even though gray iron can be hardened by quenching from elevated temperatures, heat treatment is not ordinarily used in commercial production to increase the overall strength of gray iron castings because the strength of the as cast metal can be increased at relatively lower cost by reducing the silicon and total carbon contents or by adding alloying elements. Gray cast iron itself is very brittle inherently. Moreover, hardening by quenching makes the gray cast iron tremendously very brittle. So, the most common heat treatments of gray iron are annealing and stress relieving.

Chemical composition is another important parameter influencing the heat treatment of gray cast irons. Silicon raises the austenitizing temperature significantly and reduces the combined carbon content (cementite volume). Manganese, in contrast, lowers the austenitizing temperature and increases hardenability. It also increases carbon solubility and increases the combined carbon content. In addition, manganese alloys and stabilizes pearlitic carbide and thus increases the pearlite content.

### 4.2.2 Annealing of Gray Cast Iron

The heat treatment most frequently applied to gray iron, with the possible exception of stress relieving, is annealing. The annealing of gray iron consists of heating the iron to a temperature high enough to soften it and/or to minimize or eliminate massive eutectic carbides, thereby improving its machinability. This heat treatment reduces mechanical properties substantially. It reduces the grade level approximately to the next lower grade, for example, the properties of a class 40 gray iron will be diminished to those of a class 30 gray iron. The degree of reduction of properties depends on the annealing temperature, the time at temperature and the alloy composition of the iron. Gray iron is commonly subjected to one of three annealing treatments, each of which involves heating to a different temperature range. These treatments are ferritizing annealing, medium (or full) annealing and graphitizing annealing.

#### 4.2.2.1 Ferritizing Annealing

For an unalloyed or low alloy cast iron of normal composition, when the only result desired is the conversion of pearlitic carbide to ferrite and graphite for improved machinability, it is generally unnecessary to heat the casting to a temperature above the transformation range. Up to approximately 595°C (1100°F), the effect of short times at temperature on the structure of gray iron is insignificant. For most gray irons, a ferritizing annealing temperature between 700 and 760°C (1300 and 1400°F) is recommended.

#### 4.2.2.2 Medium (Full) Annealing

It is usually performed at temperatures between 790 and 900°C (1450 and 1650°F). This treatment is used when a ferritizing anneal would be ineffective because of the high alloy content of a particular iron. It is recommended, however, to test the efficacy of temperatures below 760°C (1400°F) before a higher annealing temperature is adopted as part of a standard procedure. Holding times comparable to those used in ferritizing annealing are usually employed. When the high temperatures of medium annealing are used, however, the casting must be cooled slowly through the transformation range, from about 790 to 675°C (1450 to 1250°F).

#### 4.2.2.3 Graphitizing Annealing

If the microstructures of gray iron contain massive carbide particles, then higher annealing temperatures become necessary. Graphitizing annealing may simply serve to convert massive carbide to pearlite and graphite, although in some applications it may be desired to carry out a ferritizing annealing treatment to provide maximum machinability. The production of free carbide that must later be removed by annealing is, except with pipe and permanent mold castings, almost always an accident resulting from inadequate inoculation or the presence of excess carbide formers, which inhibit normal graphitization; thus, the annealing process is not considered part of the normal production cycle.

To break down of massive carbide with reasonable speed, temperatures of at least 870°C (1600°F) are required. With each additional 55°C (100°F) increment in holding temperature, the rate of carbide decomposition doubles. Consequently, it is general practice to employ holding temperatures of 900 to 955°C (1650 to 1750°F).

#### 4.2.2.4 Normalizing

Gray iron is normalized by being heated to a temperature above the transformation range, held at this temperature for a period of about 1 hour per inch of maximum section thickness and cooled in still air to room temperature. Normalizing may be used to enhance mechanical properties, such as hardness and tensile strength. The temperature range for normalizing gray iron is approximately 885 to 925°C (1625 to 1700°F). Austenitizing temperature has a marked effect on microstructure and on mechanical properties such as hardness and tensile strength. The tensile strength and hardness of a normalized gray iron casting depend on the following parameters:

a) Combined carbon content
b) Pearlite spacing (distance between cementite plates)
c) Graphite morphology.

The graphite morphology does not change to any significant extent during normalization and its effect on hardness and tensile strength is omitted in this discussion on normalizing. Combined carbon content is determined by the normalizing (austenitizing) temperature and the chemical

composition of the casting. Higher normalizing temperatures increase the carbon solubility in austenite (that is, the cementite volume in the resultant pearlite, Fig.4.4). A higher cementite volume, in turn, increases both the hardness and the tensile strength. The alloy composition of a gray iron casting also influences carbon solubility in austenite. Some elements increase carbon solubility, some decrease it and others have no effect on it. The carbon content of the matrix is determined by the combined effects of the alloying elements.

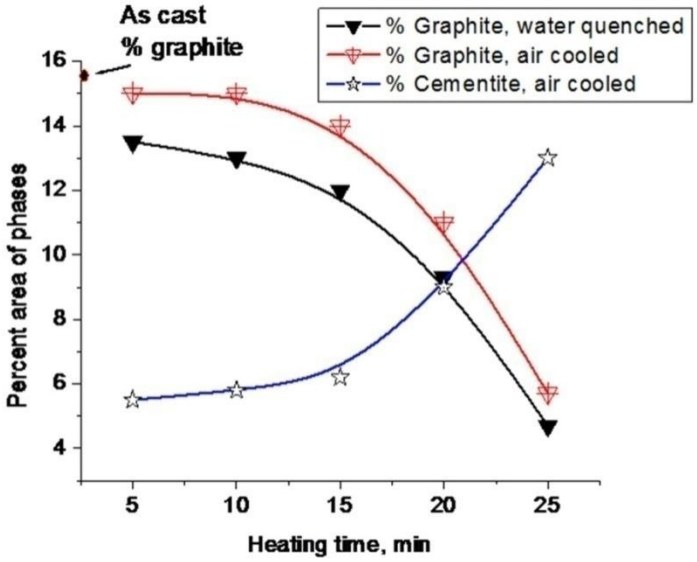



Figure 4.4: Effect of heating time in austenite zone on graphite and carbide in gray cast irons

The other parameter affecting hardness and tensile strength in a normalized gray iron casting is the pearlite spacing. Pearlite spacing is determined by the cooling rate of the casting after austenitization and the alloy composition. Fast cooling results in small pearlite spacing, higher hardness, and higher tensile strength. Too high a cooling rate may cause partial or full martensitic transformation. The addition of alloying elements may change hardness and tensile strength significantly.

### 4.3 Ductile Iron

**Ductile iron**, also referred to as nodular iron or spheroidal graphite iron, was patented in 1948. After a decade of intensive development work in the 1950s, ductile iron had a phenomenal nine-fold increase in use as an engineering material during the 1960s and the rapid increase in commercial application continues today. An unusual combination of properties is obtained in ductile iron because the graphite occurs as spheroids rather than as individual flakes as in gray iron. This mode of solidification is obtained by adding a very small, but specific, amount of Mg to molten iron of a proper composition. The base iron is severely restricted in the allowable contents of certain minor elements that can interfere with the graphite spheroid formation. The added Mg reacts with the sulfur and oxygen in the molten iron and changes the way the graphite

is formed. Control procedures have been developed to make the processing of ductile iron dependable.

The high C and Si content of ductile iron provide the casting process advantages, but the graphite spheroids have only a nominal influence on the mechanical properties of the metal. Ductile iron, like malleable iron, exhibits a linear stress strain relation, a considerable range of yield strengths and, as its name implies, ductility. Castings are made in a wide range of sizes with sections that can be either very thin or very thick. The different grades are produced by controlling the matrix structure around the graphite either as-cast or by subsequent heat treatment. Only minor compositional differences exist among the regular grades, and these adjustments are made to promote the desired matrix microstructures. Alloy additions may be made to ductile iron to assist in controlling the matrix structure as-cast or to provide response to heat treatment. Special analysis ductile irons and high-alloy ductile irons provide unusual properties for special applications. Through heat treatments, the properties of ductile irons are possible to modify a very wide range.

### 4.3.1 Heat Treating of Nodular Irons

The most important heat treatments for ductile or nodular cast irons and their purposes are:

a) Stress relieving, a low-temperature treatment, to reduce or relieve internal stresses remaining after casting.
b) Annealing, to improve ductility and toughness, to reduce hardness, and to remove carbides.
c) Normalizing, to improve strength with some ductility.
d) Hardening and tempering, to increase hardness or to improve strength and raise proof stress ratio.
e) Austempering, to yield a microstructure of high strength, with some ductility and good wear resistance.
f) Surface hardening, by induction, flame, or laser, to produce a locally selected wear-resistant hard surface.

#### 4.3.1.1 Austenitizing Ductile Cast Iron

The usual objective of austenitizing is to produce an austenitic matrix with as uniform carbon content as possible prior to thermal processing. For a typical hypereutectic ductile cast iron, an upper critical temperature must be exceeded so that the austenitizing temperature is in two phase (austenite and graphite) field. This temperature varies with alloy content. The "equilibrium" austenite carbon content in equilibrium with graphite increases with an increase in austenitizing temperature. This ability to select (within limits) the matrix austenite carbon content makes austenitizing temperature control important in processes that depend on carbon in the matrix to drive a reaction. This is particularly true in structures to be austempered, in which the hardenability (or austemperability) depends to a significant degree on matrix carbon content. In

general, alloy content, the original microstructure and the section size determine the time required for austenitizing. The sections to follow on annealing, normalizing, quenching and tempering and austempering discuss austenitizing when it is of concern.

### 4.3.1.2 Annealing

Annealing softens the ductile Iron by producing a carbide free, fully ferritic matrix. Table 4.1 given below describes recommended practices for annealing of ductile iron. These procedures range from a low temperature or subcritical annealing used to ferritize carbide free castings, to two stage and high temperature anneals designed to break down carbides.

Table 4.1: Recommended practices for nodular cast iron.

| Type of Anneal | Purpose | Temperature (a) | Time | Cooling Cycle (b) |
|---|---|---|---|---|
| Low temp. (Ferritizing) | To make carbide free and obtain Grades 60-45-12, 60-40-18 | 1325 to 1350F (720 to 730C) | 1 hr/inch$^2$ X-sec | Furnace cool (100F or 55C per hour) to 650F (345C). Air Cool. |
| Full (for lower Si content Fe) | To make carbide free and obtain Grade 60-40-18 with max. low temp. impact strength | 1600 to 1650F 870 to 900C | only to equalize at control temp. | Furnace cool (100F or 55C per hour) to 650F (345C). Air Cool. |
| High temp. (Graphitizing) | In presence of carbides to obtain Grades 60-45-12, 60-40-18 | 1650 to 1700F 900 to 925C | 2 hours min | Furnace cool (95C/hr to 700C), furnace cool (55C/ hr to 345C, then air cool. |
| Two stage Graphitizing and Ferritizing | In presence of carbidesto obtain Grades 60-45-12, 60-40-18 where rapid cooling is practical | 1600 to 1650F 870 to 900C | 1 hour per inch of cross section | Fast cool to 1250 to 675-700C, reheat to 730C for 2 hrs/inch$^2$ X-sec, air cool. |

The microstructures of as cast (left and middle) and annealed ductile iron are presented in the following Fig.4.5.

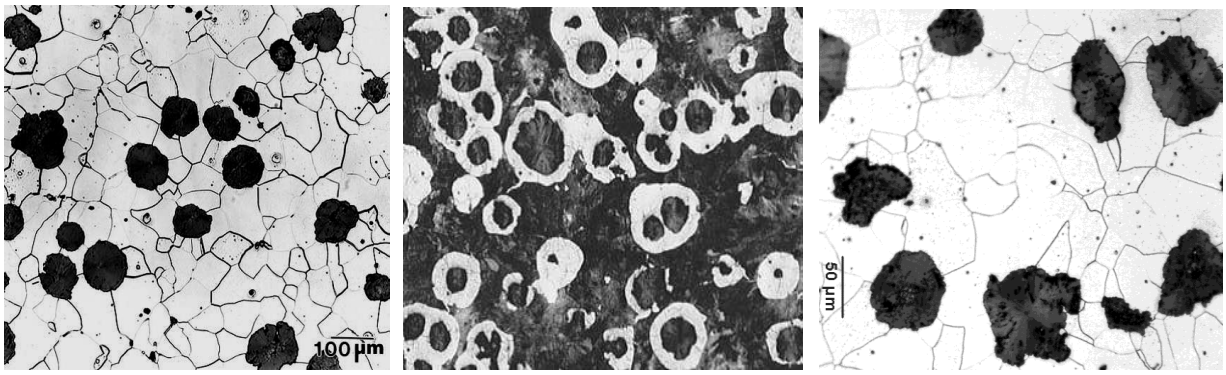



Figure 4.5: Microstructures of as cast (left and middle) and annealed (right) nodular cast irons.

It is important to realise that in most cases, the mechanical properties of cast iron is dependent on C and Si content and that the comparison between microstructures and mechanical properties is

non-linear. However, the relationship is more linear when the pearlite content is less than ~20%. In such case, UTS and YS can be calculated from the following relationships:

$$\textbf{Yield Strength (MPa)} = 52 + 63{\cdot}2\times[\%Si] + 0{\cdot}663X_p + 21{\cdot}6(1-0{\cdot}0656\times[\%C])d^{-0{\cdot}5}$$

$$\textbf{UTS (MPa)} = 147 + 68{\cdot}1[\%Si] + 1{\cdot}77X_p + 26{\cdot}7(1-0{\cdot}0656[\%C])d^{-0{\cdot}5}$$

Here $X_p$ is the percentage of pearlite and d is the diameter of ferrite grains.

The primary purpose of annealing or ferritizing of ductile iron is the production of castings with maximum ductility and toughness, reduced strength and hardness, improved machinability and uniform properties.

### 4.3.1.3 Normalizing

Normalizing involves the austenitizing of a ductile iron casting, followed by cooling in air through the critical temperature. An as cast ductile iron casting is normalized in order to: break down carbides, increase hardness and strength and produce more uniform properties. Normalizing should be carried out at an austenitizing temperature approximately 100°C above the critical temperature range. Typically, austenitizing temperatures in the range 875-900°C and holding times of one hour, plus one hour per inch of casting thickness, are adequate to produce a fully austenitic structure in unalloyed castings relatively free of carbide. The cooling rate should be sufficiently rapid to suppress ferrite formation as much as possible. In this respect, the continuous cooling curves for ductile iron should be consulted properly, Fig.4.6.

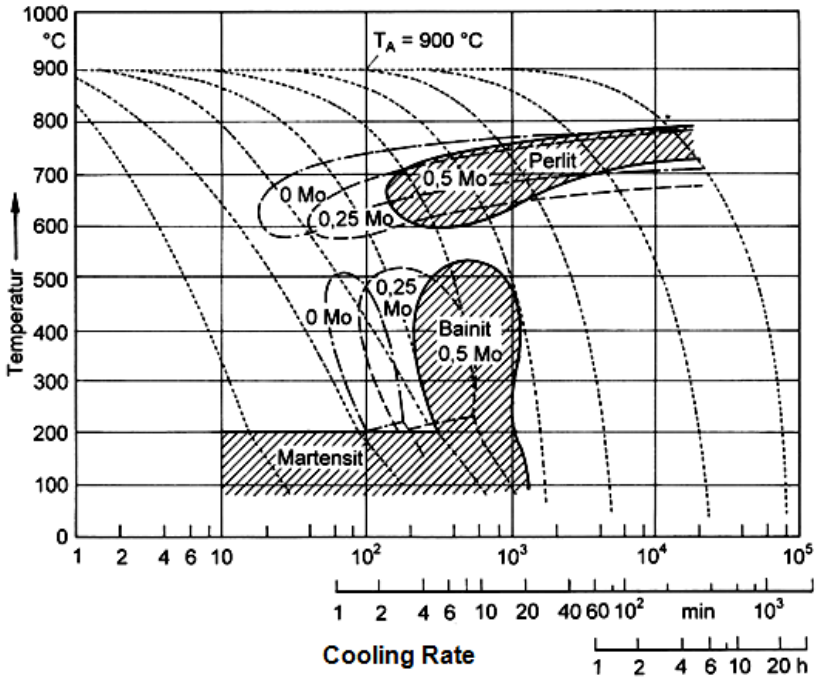



Figure 4.6: Continuous cooling curves for ductile iron.

Depending on casting section size and alloy content, adequate cooling rates can be achieved in still air or large fans may be required. If fan cooling cannot produce the desired pearlitic structure, the castings should be alloyed with pearlite stabilizing elements such as copper, tin, nickel or antimony. It is to be noted that with increase in pearlite content, strength increases but ductility decreases, Table 4.2.

Table 4.2: Structure-property relationship of nodular cast iron.

| (Ferrite+Pearlite)% | UTS, MPa | YS, MPa | %El |
|---|---|---|---|
| 0+100 | 804 | 416 | 8 |
| 30+70 | 664 | 339 | 11 |
| 60+40 | 488 | 310 | 15 |

There is strong influence of silicon on the carbon solubility in austenite of ductile iron. With increase in silicon content and decrease in austenitizing temperature, Si solubility in austenite decrease, Fig.4.7.

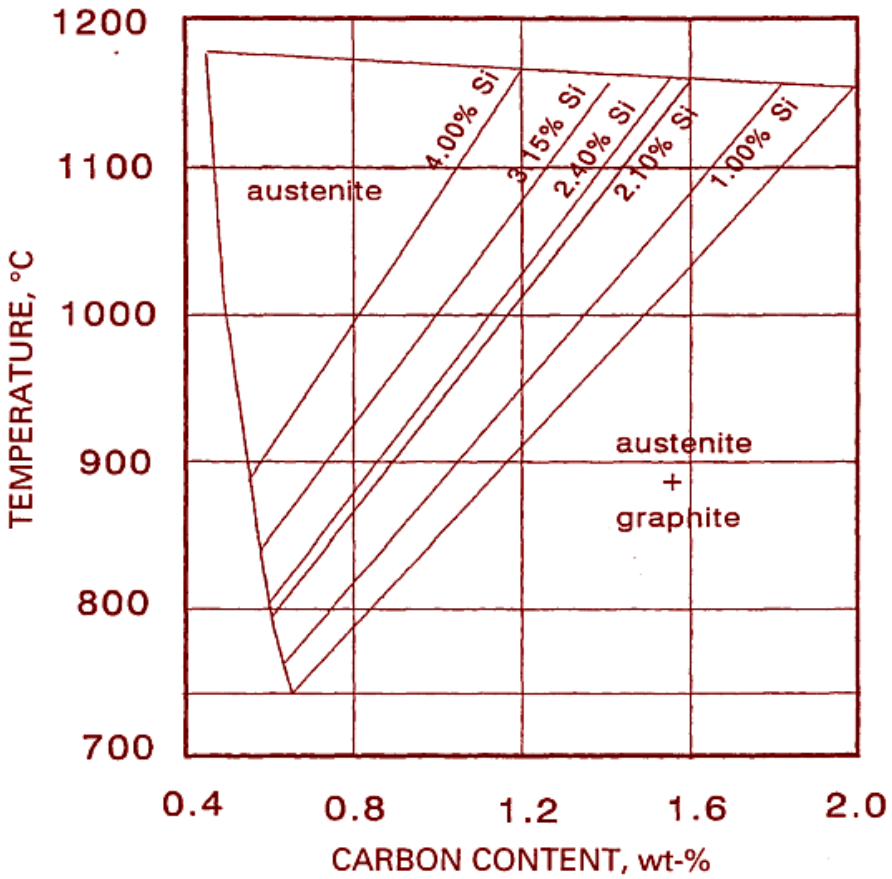



Figure 4.7: Effects of Si content on carbon solubility of in austenite.

As the carbon solubility in austenite decreases with silicon content, so the pearlite content in the ductile iron also decreases. So, with silicon content the strength of cast iron decreases. For quantitative measurement of combined carbon in ductile iron the following relationship can be used.

$$\%C_0 = \frac{T_\gamma}{420} - 0{\cdot}17\text{Si} - 0{\cdot}95$$

Here $T_\gamma$ is the austenitizing temperature for normalizing heat treatment.

### 4.3.1.4 Quench Hardening

Maximum hardness in nodular cast iron (NCI) castings is obtained by austenitizing, followed by quenching sufficiently rapidly to suppress the formation of both ferrite and pearlite where austenite transforms to martensite at lower temperature. Hardness of as quenched nodular cast iron depends on the carbon content of the martensite and the volume fraction of martensite in the matrix. In conjunction with the silicon content, the austenitizing temperature determines the carbon content of the austenite. For a silicon content of approximately 2.5%, an austenitizing temperature of 1650°F (900°C) will result in the optimum carbon content and maximum hardness, Fig.4.8.

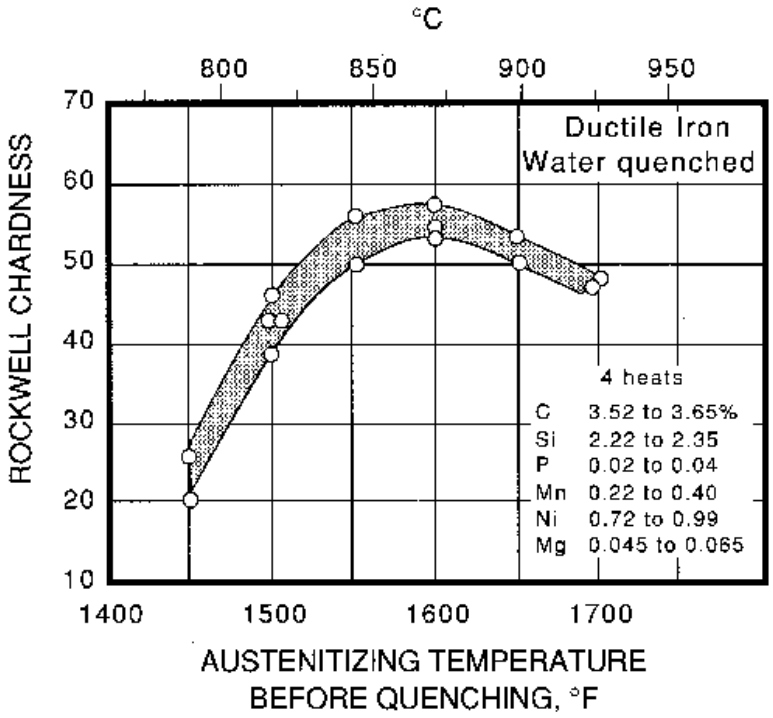



Figure 4.8: Effects of austenitizing temperature on the hardness values of quenched nodular cast irons.

Lower temperatures, 1475-1550°F (800-845°C), will produce a low carbon austenite which, on cooling, will transform to a softer martensite. The microstructure of nodular cast iron after full austenitization and quenching is shown below in Fig.4.9.

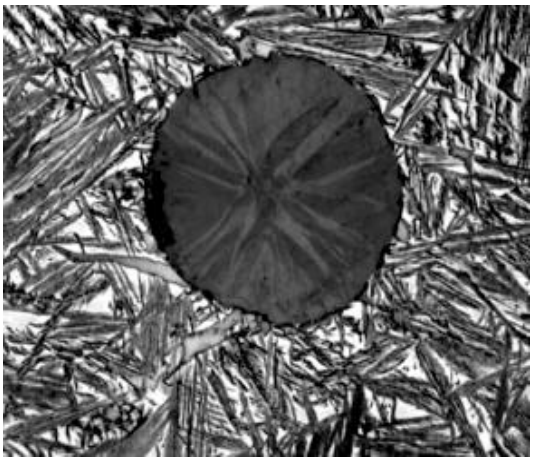


Figure 4.9: As quenched martensitic microstructure of nodular cast irons.

The effect of austenitizing temperature on microstructures (%martensite) is shown below in Fig.410. Higher austenitizing temperature ensures more martensite (right).

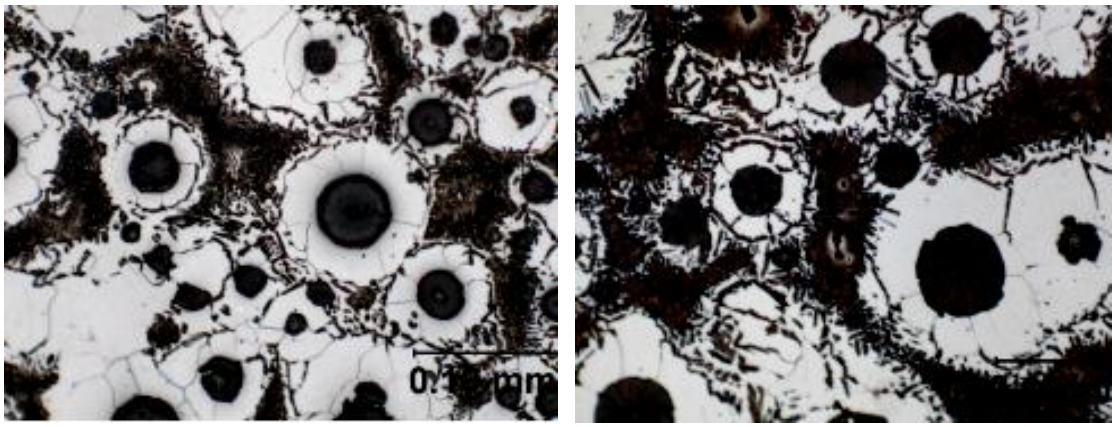


Figure 4.10: Tempered martensite in NDI austenitized at relatively low (left) and high (right) temperatures.

The formation of low carbon martensite will cause reduced distortion and cracking in complex castings during quenching and when tempered, low carbon martensite has toughness superior to both tempered high carbon martensite and normalized microstructures. Very higher austenitizing temperatures increase the carbon content of the austenite but the bulk hardness is reduced due to retained austenite and a lower resultant martensite content. Regardless of the austenitizing and quenching conditions, quenched ductile iron castings must be tempered before use to eliminate internal stresses, control strength and hardness and provide adequate ductility.

**4.3.1.4 Hardenability of NCI**

Hardenability is a measure of how rapidly the ductile iron casting must be cooled in order to suppress the ferrite and pearlite transformations and produce a martensitic, bainitic or austempered matrix. Hardenability is an important property of any casting that is to be quench hardened because it determines the depth to which a fully or partially martensitic matrix can be

produced and the severity of quench required to harden castings of different section size. The effects of various alloying elements on the hardenability of ductile iron are illustrated in the following Fig.4.10.

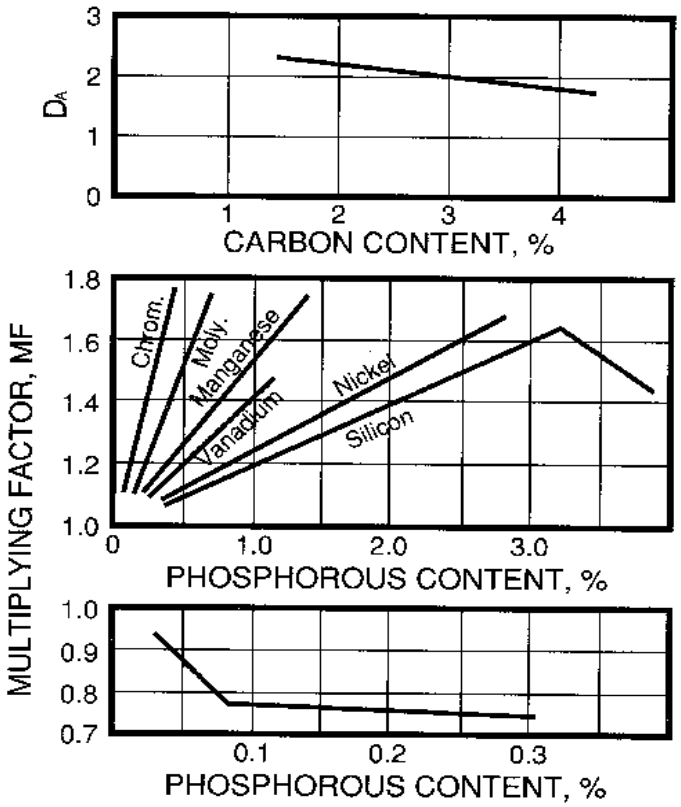



Figure 4.10: Effects of various alloying elements on the hardenability of nodular cast irons.

To calculate the hardenability of a casting the absolute hardenability ($D_A$), based on the carbon content, is first determined. The ideal critical diameter ($D_I$) is then calculated by multiplying $D_A$ by the multiplying factors determined as per chemical compositions, Table 4.3.

Table 4.3: Effects of alloying elements on hardenability of NCI.

| | | | |
|---|---|---|---|
| Total Carbon, % | 3.60 | $D_A$ | = 2.00 |
| Silicon, % | 2.50 | MF | = 1.50 |
| Manganese, % | 0.35 | MF | = 1.15 |
| Phosphorous, % | 0.07 | MF | = 0.80 |
| Nickel, % | 1.00 | MF | = 1.25 |

The ideal critical diameter would be calculated as follows:

$$\mathbf{D_I = D_A \times (MF_{Si}) \times (MF_{Mn}) \times (MF_P) \times (MF_{Ni}) = 3.45 \text{ inches } (88 \text{ mm})}$$

Alloying elements for quenched and tempered ductile Iron should not be selected on the basis of hardenability alone. Chromium, which is extremely effective in promoting hardenability, is very detrimental to ductile iron quality because it increases the formation of carbides in the as cast state. Manganese not only promotes the formation of carbides but also retards the tempering process. Thus, for both metallurgical and economic reasons, alloying elements should be selected carefully and used at the lowest levels which provide the desired hardenability.

**4.3.1.5. Tempering**

Tempering reduces the strength and hardness and increases the ductility, toughness and machinability of quenched or normalized ductile iron. In addition, tempering quenched castings also reduces residual stresses, decreases the amount of retained austenite and reduces the probability of cracking. These changes in properties are achieved by holding the castings at a temperature that is below the critical temperature. Tempering is a diffusional process and thus is time and temperature dependent. Tempering conditions are influenced strongly by the desired change in properties, the alloy content, the microstructure being tempered and the nodule count. Low alloy content, martensitic structures and high nodule count reduce tempering temperatures and/or times, while high alloy content, a normalized (pearlitic) structure and low nodule count increase tempering times.

During tempering breakdown of the martensite needles takes place (Fig.4.11) and the residual stress is released. This enhances the mechanical properties of the ductile irons.

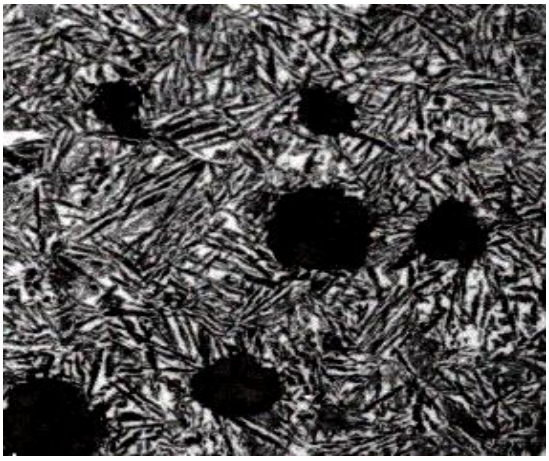


Figure 4.11: Microstructures of tempered martensite of nodular cast irons.

**4.3.1.6 Temper Embrittlement**

Temper embrittlement, a type of embrittlement found in certain quenched and tempered steels, may also occur in similarly treated ductile irons with susceptible compositions. This form of embrittlement, which does not affect normal tensile properties but causes significant reductions in fracture toughness, can occur in ductile irons containing high levels of silicon and phosphorus which have been tempered in the range 650-1100$^{o}$F (350-600$^{o}$C) and cooled slowly after

tempering. Although normally associated with tempered martensite, temper embrittlement can also occur if the matrix is tempered to the fully ferritic condition. Temper embrittlement can be prevented by keeping silicon and phosphorus levels as low as possible, adding up to 0.15% molybdenum and avoiding the embrittling heat treating conditions.

### 4.3.1.7 Secondary Graphite

The formation of secondary graphite during the tempering of martensitic ductile iron can be responsible for both the degradation and increased variability of mechanical properties. Secondary graphitization is favoured by low austenitizing and tempering temperatures and high levels of silicon, copper and nickel. Like temper embrittlement, the use of small additions of molybdenum can eliminate this problem. To further prevent its occurrence, the tempering of martensitic ductile irons to hardness below 270 BHN, which require high temperature tempering, should be avoided.

### 6.3.1.8 Austempering of Ductile Iron

In recent years, austempered ductile iron (ADI) has attracted considerable interest because of its excellent properties, such as resistance to fatigue, good wear resistance, high strength with good ductility and rolling contact resistance. The manufacturing cost of ADI is also substantially lower than wrought or forged steel. Furthermore, the density of ADI is lower than steel. Thus, ADI has the advantage of higher specific strength than steel. Due to all the stated properties of ADI above, it is considered a very promising engineering material and an economical substitute for wrought or forged steel in several structural applications in the automotive industry.

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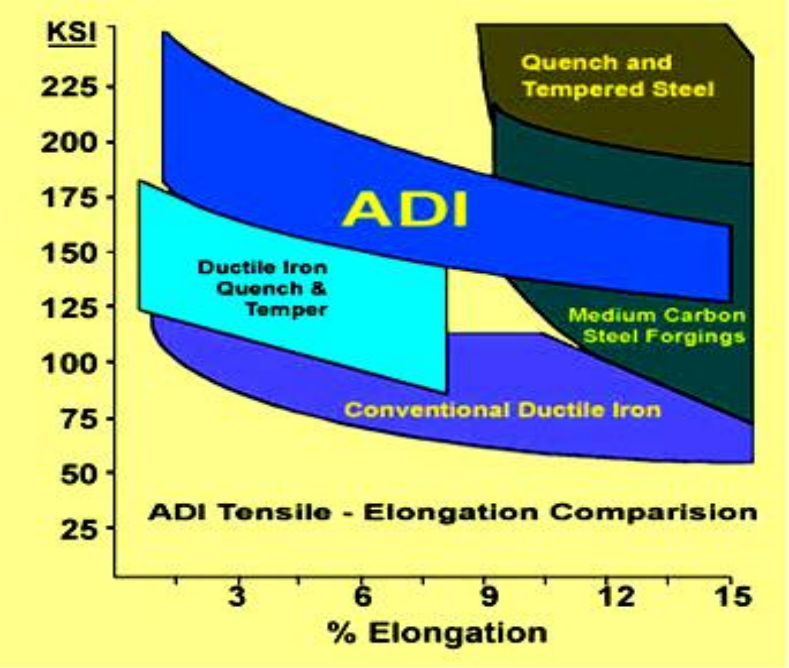



Figure 4.12: Tensile strength and elongation comparison for various ferrous alloys.

The mechanical properties of ADI can be tailored to suit particular applications by adjusting heat treatment parameters or material compositions, which might be comparable hardened tempered steels and much better than medium carbon forged steels, Fig.4.12. In ADI, the property enhancement is aided by proper controlling in the proportion of the phases present in the microstructures. The process is very simple that involves the production of a ductile iron casting, austenitization at (800-950$^{o}$C) in salt bath with potassium chloride, sodium chloride and barium chloride and then quenching to a temperature (250-400$^{o}$C) in salt bath of potassium nitrate and sodium nitrate, Fig.4.13.

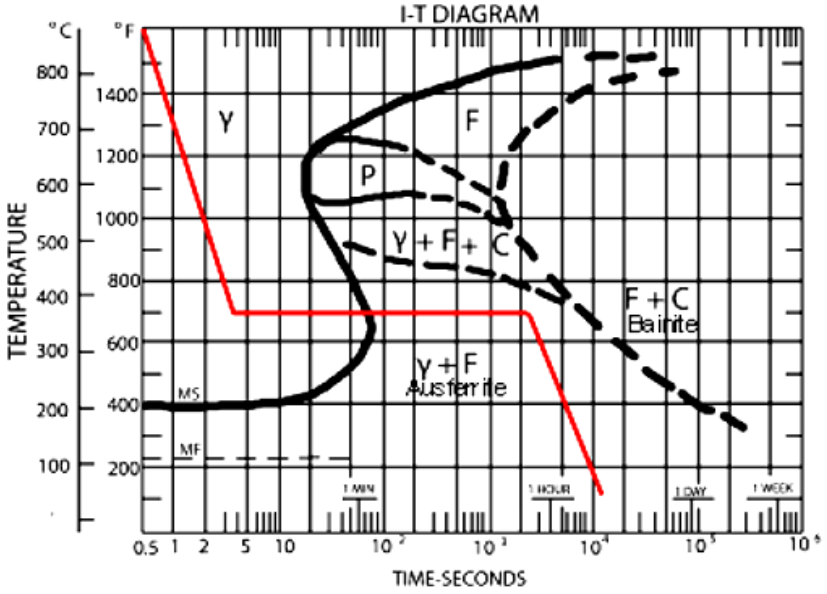



Figure 4.13: Isothermal cooling curve for austempering of ductile iron.

The most surprising example is the truck wheel made from ADI which is lighter than that from forged steel. Compared to the conventional grades of ductile iron, ADI delivers twice the strength for a given level of ductility in the form of elongation, Fig.4.12. The optimum combination of high carbon austenite and bainitic ferrite of ADI makes it possible to compete against steel forgings and other engineering alloys in terms of mechanical properties, physical properties, weight saving and all that at low cost. ADI offers superior combination of properties because it can be cast like any other member of the ductile iron family, thus offering all the production advantages of a conventional ductile iron casting. The ductile Iron casting is subsequently subjected to the austempering process to produce mechanical properties that are superior to conventional ductile iron and forged steel. Improved toughness of ADI results from:

1. reduced ferrite particle size,
2. increased carbon content in the retained austenite, which increases the strain hardening ability and strain hardening coefficient and
3. stability of the retained austenite

It has been well documented that the mechanical properties ADI is much more superior than that could be achieved by any heat treatment of the ductile iron and the resulted microstructure is shown in Fig.4.14.

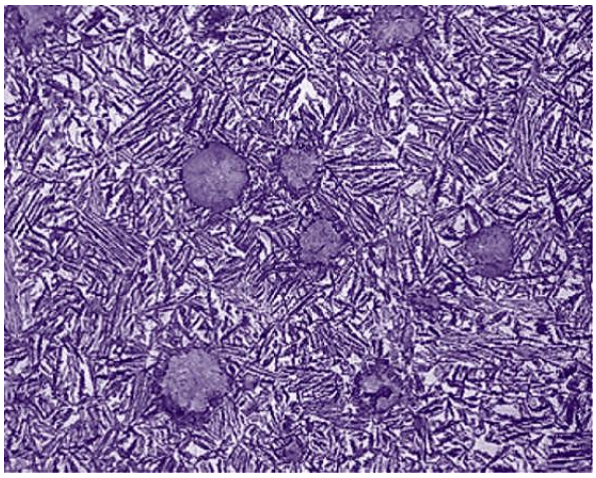


Figure 4.14: Microstructures of austempered ductile iron.

After full austempering, the yield strength of the ADI may be calculated from the following empirical relationship:

$$\sigma\ (\text{MPa}) = \sigma_o + 1722\ (\%C)^{1/2} + 115d^{-1} + 7.34\text{x}10^{-6}\rho$$

The first term ($\sigma_o$) represents the intrinsic contribution of the pure iron in a fully annealed condition (~175MPa). The second term takes into account the strengthening due to the carbon dissolved in interstitial solution of bainitic ferrite (0.03%). The third term corresponds to the lath size effect, *d* is the width expressed in mm. Finally, the effect of the dislocation density, $\rho$, generated by the transformation condition. This can be expressed, over the temperature range 570 to 920K as:

$$\log\ (\rho) = 9.2840 + \frac{6880.73}{T} - \frac{1{,}780{,}360}{T^2}$$

For approximate UTS calculation the yield is multiplied by 1.45.

### 3.4 Malleable Cast Iron

These are produced from white cast irons modified by malleabilizing heat treatment. The produced cast irons provide better strength along with significant improvement in ductility. As a result, this cast iron is named by the heat treatment process used. The heat treatment consists heating the white cast iron slowly to a temperature at around 900$^{o}$C and holding at this temperature for long time followed by cooling to room temperature, Fig.4.15.

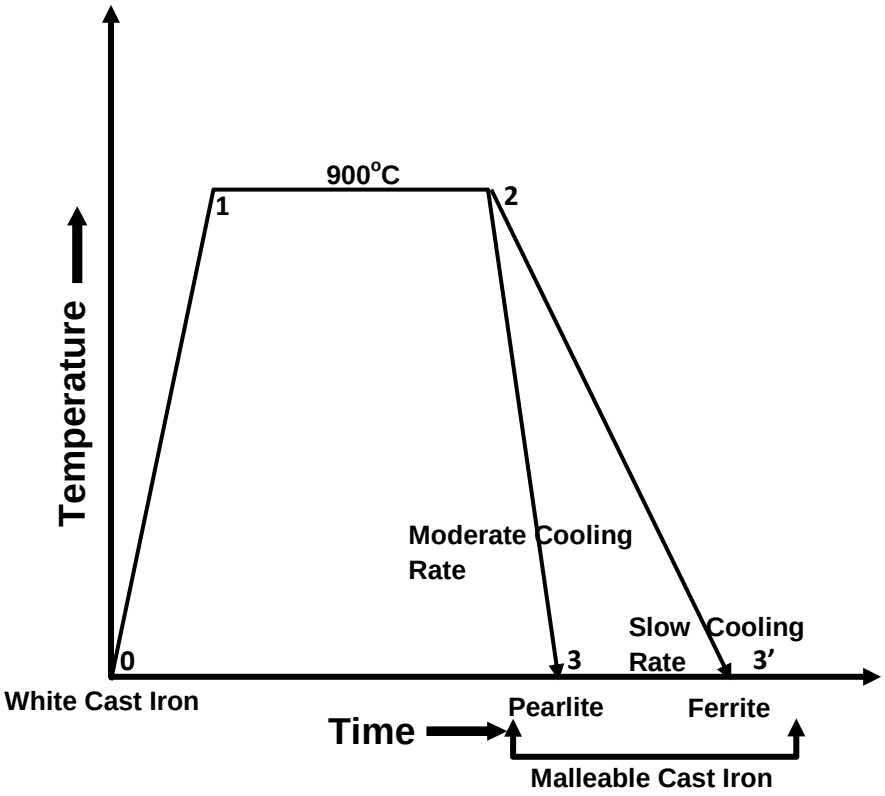



Figure 4.15: Heat treatment cycle for the production of malleable cast iron.

In the above heat treatment cycle (Fig.4.15), 0-1 denotes slow heating period. On heating, pearlite and part of cementite transform to austenite. During long time holding period (1-2) cementite phase is converted to graphite, which exists in the form of clusters or rosettes around austenite. In the next step when this structure is cooled, where cluster form of graphite does not change, but the austenite transforms to either pearlite or ferrite depending on cooling rates. For faster cooling (2-3) pearlitic or white heart malleable cast iron is formed. On the other hand, if the cooling rate is very slow (2-3'), more carbon from austenite will come out and rest of the austenite transforms to ferrite, which is called black heart malleable cast iron, Fig.4.16. Depending on heat treatment parameter, chemical compositions of the initial white cast irons mixed type microstructures (ferrite-pearlitic) of the malleable cast iron might also form in the heat treated product, i.e. in malleable cast irons. The chemical compositions of a typical malleable cast iron are presented in the following Table 4.4.

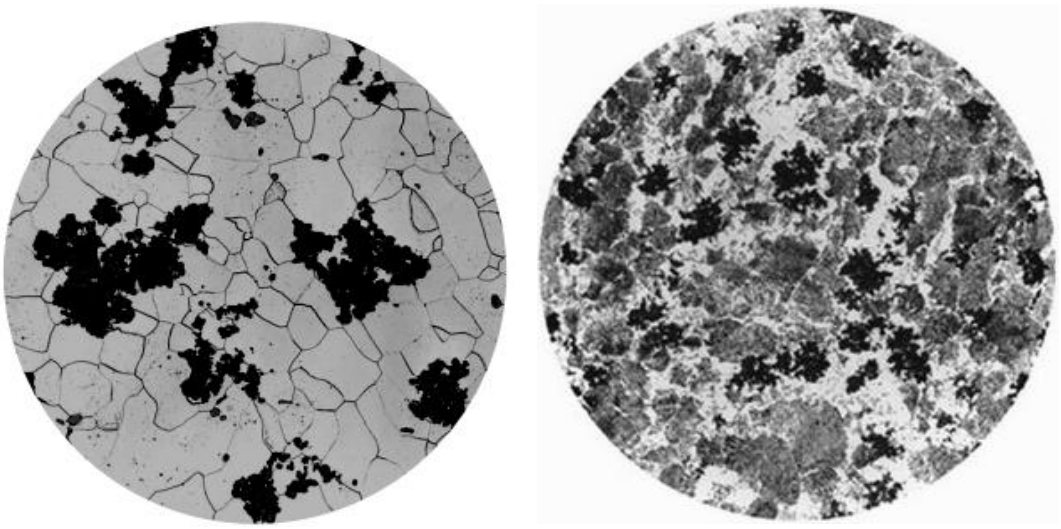


Figure 4.16: Microstructures of ferritic and (black heart, left) and pearlitic (white heart, right)

Table 4.4: Chemical compositions of malleable cast iron.

| |
|---|
| **Carbon: 2.00-2.65 Silicon: 0.90-1.40% Manganese: 0.25-0.55% Phosphorus: <0.18% Sulphur: 0.05%** |

Table 4.5: Mechanical properties of malleable cast iron.

| Grade | Composition (Weight%) | Matrix Structures | TS (MPa) | YS (MPa) | % Ductility (50mm GL) | Typical Applications |
|---|---|---|---|---|---|---|
| 32510 | 2.3.-2.7C<br>1.0-1.75Si<br><0.55Mn | Ferrite | 345 | 224 | 10 | Various tool for general engineering service at normal and elevated temperatures |
| 45006 | 2.4.-2.7C<br>1.25-1.55Si<br><0.55Mn | Ferrite<br>+<br>Pearlite | | 310 | 6 | Relatively stronger tools for general engineering service at normal and elevated temperatures |

After heat treatment processes, malleable iron can be shaped through cold working, such as stamping for straightening, bending or coining operations. This is possible due to malleable

iron's desirable property of being less strain rate sensitive than other materials. The mechanical properties of some malleable cast irons are mentioned in the following Table 4.5.

Malleable iron also exhibits better fracture toughness properties in low temperature environments than other nodular irons, due to its lower silicon content. The ductile to brittle transformation temperature is lower than many other ductile iron alloys. It is often used for small castings requiring good tensile strength. It has a wide range of applications. Some of which are as electrical fittings, gears, weight blocks, hand tools, pipe fittings, washers, brackets, fence edfittings, power line hardware, farm equipment, mining hardware and machine parts, Figure 4.17.

Figure 4.17: Various parts and equipment made from malleable cast iron.

# Chapter Five

## Heat Treatment of Tool Steels

### 5.1 Introduction

Tool steel refers to a variety of carbon and alloy steels that are particularly well-suited to be made into tools. Although the development of modern tool steel began in the second half of the 19th century, there is documented evidence of steels produced earlier with similar content. These include hardened steels in China in 13th century BC, wootz steel manufactured in India around 350 BC and production of Damascus and Japanese layered steel blades in years 540 AD and 900 AD. High-speed cutting properties of some of these steels would be mostly coincidental (as no machining technology that involved quantification of speeds and feeds existed at the time) and would be the result of local iron ores containing natural traces of tungsten or other favorable alloying components.

In 1868 the English metallurgist Robert Forester Mushet developed Mushet steel, considered to be the forerunner of modern high-speed steels. It consisted of 2% carbon (C), 2.5% manganese (Mn) and 7% tungsten (W). The major advantage of this steel was that it hardened when air cooled from a temperature at which most steels had to be quenched for hardening. Over the next 30 years, the most significant change was the replacement of manganese (Mn) with chromium (Cr). In 1899 and 1900, Frederick Winslow Taylor and Maunsel White, working with a team of assistants at the Bethlehem Steel Company at Bethlehem, Pennsylvania, US, performed a series of experiments with the heat treating of existing high-quality tool steels, such as Mushet steel, heating them to much higher temperatures than were typically considered desirable in the industry. Their experiments were characterized by a scientific empiricism in that many different combinations were made and tested, with no regard for conventional wisdom or alchemic recipes, and with detailed records kept of each batch. The end result was a heat treatment process that transformed existing alloys into a new kind of steel that could retain its hardness at higher temperatures, allowing much higher speeds and rate of cutting when machining.

The suitability of tool steels comes from their distinctive hardness, resistance to abrasion and deformation and their ability to hold a cutting edge at elevated temperatures. As a result, tool steels are suited for use in the shaping of other materials. With carbon content between 0.5% and 1.5%, tool steels are manufactured under carefully controlled conditions to produce the required quality. The presence of carbides in their matrix plays the dominant role in the qualities of tool steel. The four major alloying elements that form carbides in tool steel are: tungsten, chromium, vanadium and molybdenum. The rate of dissolution of the different carbides into the austenite form of the iron determines the high-temperature performance of steel (slower is better, making for a heat-resistant steel). Proper heat treatment of these steels is

important for adequate performance. The manganese content is often kept low to minimize the possibility of cracking during water quenching.

The heat treatment to harden tool iron, consisting of heating and water quenching was known from long time ago. The earliest tool steels were based on plain carbon steel. In the mid-19th century and early in the 20th century, highly alloyed tool steels were developed to meet very stringent requirements for specific applications. This evolution was taking place in parallel with the understanding of the benefit of the alloying elements such as manganese, tungsten, molybdenum, vanadium and chromium and their availability. In parallel to this evolution, steel making evolved toward more controlled conditions to improve the quality and cleanliness of the tool steels. This advance in technology and knowledge allows designing specialized tool steels for cold and hot working of metals, moulding plastics, as well as for many other special purposes. This chapter reviews heat treatment of various types of tool steels to achieve the required properties for specific applications.

## 5.2 Property Requirement for Tool Steels

Tool steels are high quality steels as opposed to construction steels, for which new steel grades are developed more economically with mechanical properties obtained directly from forging or rolling. The Mechanical property of tool steels requires very highly controlled heat treatments. The microstructure and properties of tool steels resulting from heat treatment depend on the chemical composition for a given grade and on the annealing conditions. Tool steels are used for many applications dealing with manufacturing. Their field of application includes machining, cutting, forming by stamping, pressing or forging, forming of shapes from the molten stat e in glass, plastics, or metals, and die casting. Their characteristics cannot be found simply from their chemical compositions only. The important properties of tool steels are constant hardness at low and high temperatures, hardenability, retention of hardness, high compressive strength and pressure resistance, fatigue strength, toughness at operational temperatures, wear resistance at room and high temperatures, thermal fatigue resistance, and corrosion resistance.

**5.2.1 Resistance to Wear** For any operation, there is relative motion, i.e. abrasion between the tool and the workpiece. So, the tool steel must have abrasion resistance sufficiently. The resistance to wear is the resistance to abrasion. This property is, in general, related to the hardness of the steel, i.e., as the hardness increases, the resistance to wear and abrasion increases. As the hardness of the hardened steel mainly depends on the carbon content of the steel, high carbon steels have good resistance to wear and abrasion. As the hardness of carbides of alloying elements like tungsten, chromium, vanadium, and molybdenum is higher than martensite, or even cementite, the presence of these elements as carbides in steels further improves the resistance to wear and abrasion. The effects of hardness of some tool steels on wear rate is shown in Fig.5.1

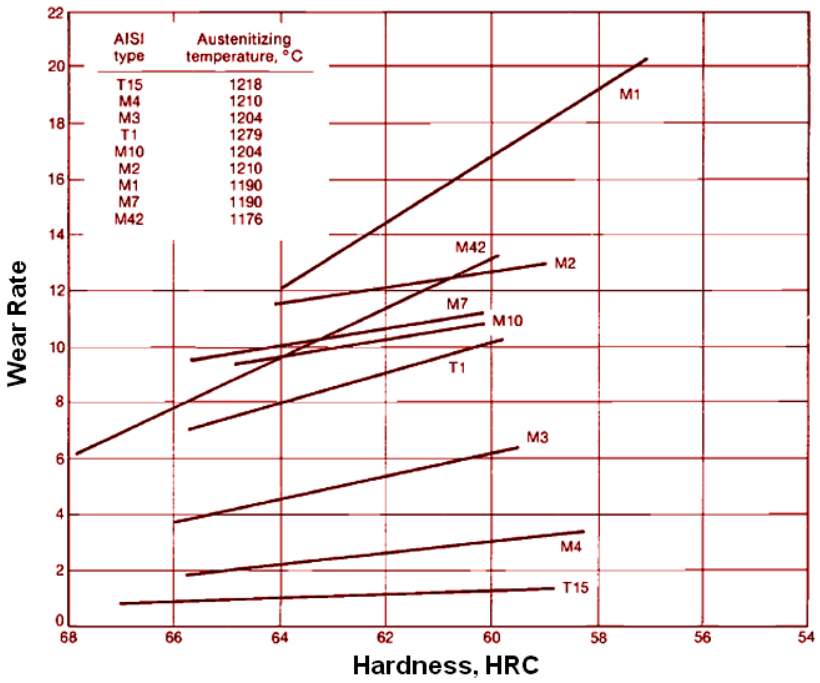


Figure 5.1: Effect of hardness on wear rate of tool steel.

### 5.2.2 Hardness

Higher hardness means lower tool wear and better service life, Fig.5.1.The hardness of tool steels is related to the material to be processed. It varies between about 200HV for glass mould steels at the lower level and 900HV for forming and machining tools at the upper level. Obtaining high hardness and microstructures that have high hardness are the major objectives of final heat treatment applied to tool steels. Carbon content is the dominant factor controlling the strength of martensite through its interaction with other structural elements of a martensitic microstructure, Fig.5.2. Martensite transformation from austenite during hardening is never complete. Hardness is the most important characteristic of tool steels that indicates their potential applications. The hardness also allows to draw a conclusion on the working stress limit and thus, on the shape stability of a tool. Due to this shape stability, hardness must be sufficiently high that the yield stress is above the highest load stress on the tool. The relationship between hardness and flow stress in the case of tool steels is shown in Fig.5.3.

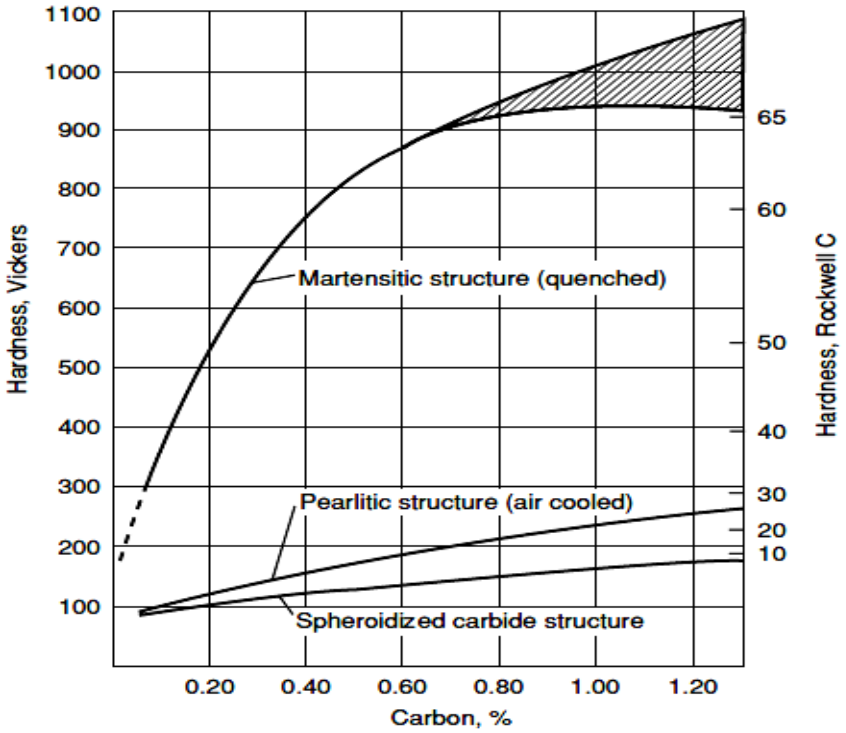



Figure 5.2: Effects of heat treatment and carbon content on hardness of various tool steels.

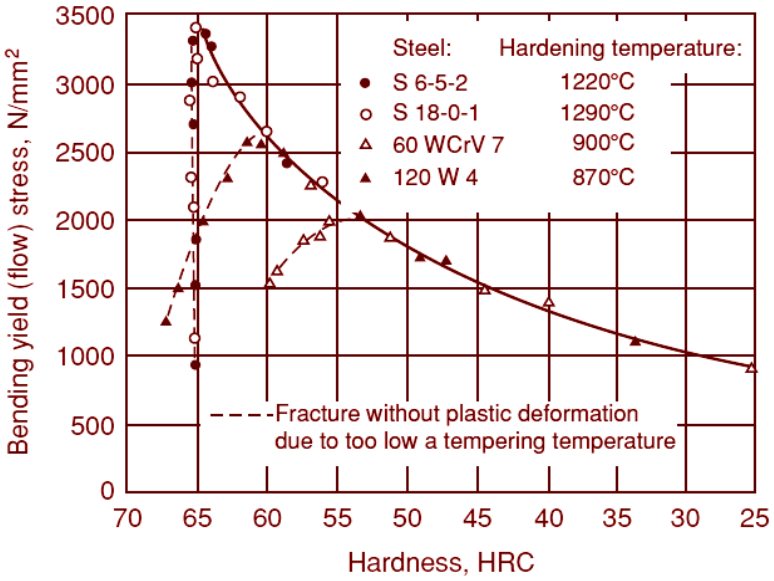

Steel: Hardening temperature:
S 6-5-2 1220°C
S 18-0-1 1290°C
60 WCrV 7 900°C
120 W 4 870°C
Fracture without plastic deformation due to too low a tempering temperature
Bending yield (flow) stress, N/mm²
Hardness, HRC

Figure 5.3: Effect of hardness on the bending yield stress of tool

All alloying elements added to the tool steels increase their hardness. Among these, Cr is the element that has less influence on the hardness enhancement, Fig.5.4. However, for tool steels this approach is not sufficient for service requirements. I such cases, the most effective way of improving hardness is through martensite formation during quenching and the precipitation of fine carbides of M o, Cr and V.

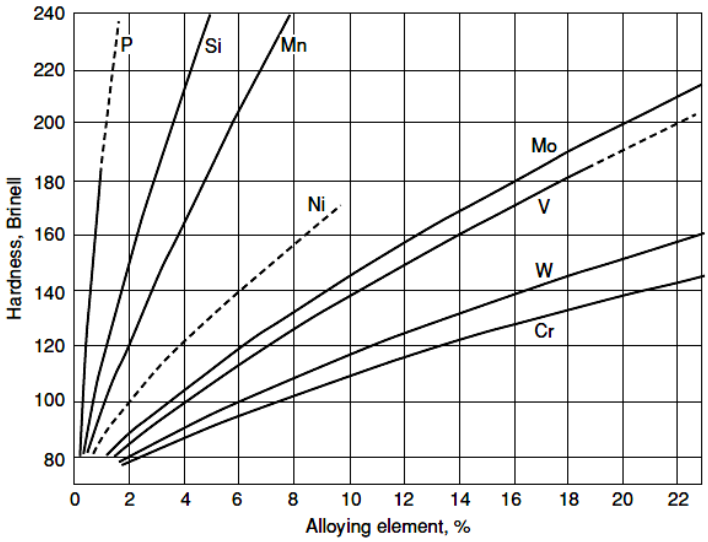



Figure 5.4: Effects of various alloying elements on hardness of steels.

### 5.2.4 Hardenability

Hardenability, which is of equal importance as hardness, includes maximum achievable hardness during quenching and the depth of hardening obtained by quenching in a specific manner. With the same hardness, a tempered martensite has better toughness than a bainitic or pearlitic microstructure. Steels for forging and pressing dies and for cutting tools need a thin surface zone with very high surface hardness but with a soft core. These steels are used in tools subjected to bending or impact, due to their lack of susceptibility to cracking. Alloying elements that stabilize austenite increase hardenability. However, with tool steels the choice of alloying elements depends on many other properties such as carbide formation, carbide hardness, decarburization tendency, nitridability and deformability. The following examples illustrate the effects of some alloying elements: (1) adding Ni gives good hardenability without carbide formation but with lower transformation temperature; (2) Si increases the tendency of decarburization; and (3) Cr, Mo, W and V result in carbide formation and make the steels easy to nitride. In tool steels, carbide quantities are up to 5 vol.% in hot work tool steels, up to 20% in high speed tool steels, and up to 25 vol.% in ledeburitic steel with 12%Cr. With C content above 0.7%, the result of increasing the hardening temperature produces a more stable austenite, which results in large quantities of retained austenite and therefore the hardness is decreased.

### 5.2.4 Toughness

The toughness of tool steels means resistance to breakage. This property is of prime importance in all cutting tools. Because shock-resisting and hot worked tool steels. As the carbon content of steel increases, (as well as vanadium) brittleness increases and toughness decreases. Thus, hot-forging dies are made, of hypo- eutectoid steels. A proper balance of silicon and other elements results in proper combination of toughness and hardness to obtain good shock-resisting steels. Almost all tools are subjected to dynamic stress peaks at a very small local cutting point from

which crack formation starts where this property of the tool steel resists such cracking. Toughness is associated with plastic deformation that prevents the crack formation. In this point of view tools of high toughness might deform during working. However, for tool steels this is not true because of very special their very features. For identical hardness level, experimental results reveal that, in general, tools of higher toughness exhibits lower wear rates, Fig.5.5. Through optimization in chemical compositions, and microstructural morphology and homogeneity better toughness can be ensured. Finer spheroidized carbides also improve toughness. It is improved by segregation reduction, cleanliness and reduction of volume fraction of inclusion (such as oxides, sulphides and carbides) and their sizes.

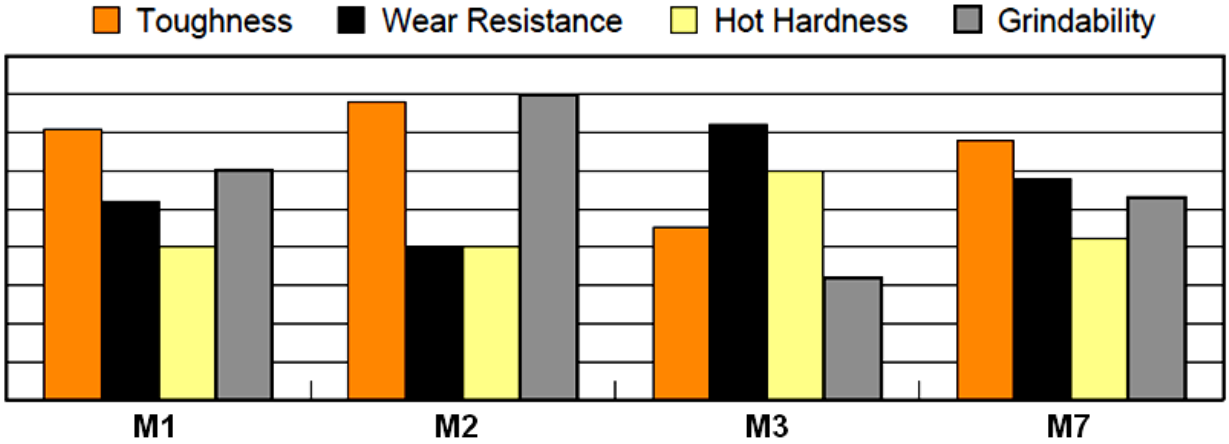



Figure 5.5: Effect of toughness on wear resistance to various tool steel of harness level 65HRC.

### 5.2.6 Red Hardness or Hot-Hardness:

It is the resistance to softening when the steel gets heated to temperatures higher than 400°C. The presence of this property in steels is reflected by a peak in the hardness versus tempering temperature curve above this temperature. Plain carbon steels and low alloy tool steels lose their hardness, and thus, the cutting edges when get heated above 200°C. Steels having alloying elements which form hard and stable carbides increase the resistance to softening at elevated temperatures (even when the steel tool tip becomes red-hot). Very finely dispersed precipitates of carbides of tungsten, vanadium, molybdenum and chromium give rise a peak in hardness curve when tempered at 550°C, called secondary hardening, and is the cause of red hardness in these steels.

### 5.2.7 Resistance to Thermal Fatigue

The failure of material by heat checking is caused by the creep behaviour of tool steels. Steels that are used for forging tools, pressure casting dies, glass forming and plastic moulds are subjected to thermal cycling during which heat checking is caused. The formation of these cracks is delayed by the use of materials with a high yield strength and high toughness at elevated temperatures. The propagation of heat checking is connected with oxidation processes. It is then important to use chromium alloyed steel s because chromium improves the scaling resistance. At higher tool temperatures, such as those sustained by a glass forming moulds, the chromium

content should be higher. The resistance to heat checking can be improved by using steels with high thermal conductivity. It is advantageous to use steels with a homogeneous quenched and tempered microstructure.

### 5.3 Classification and Selection of Tool Steels

Tool steels have been organized into groups that have evolved to perform specific functions, such as forging, cold working, die casting and high speed machining, in a variety of operating conditions. Within each group may be many grades that differ slightly from one another to accommodate somewhat different processing requirements, operating conditions or work materials. Various systems are used to classify tool steels. The most widely used system was developed by the American Iron and Steel Institute (AISI, Table 5.1). It arranges tool steels into groups (main groups are given below with symbols) that are based on prominent characteristics such as alloying, application or heat treatment. Table 5.1 lists nine main groups of tool steels and their identifying letter symbols. Other independent classification systems for tool steels from other countries such as Germany, Japan, Great Britain and France also exist.

Table 5.1: Designation of various tool steels.

| Defining property | AISI-SAE grade | Significant characteristics |
|---|---|---|
| Water-hardening | W | Water Quench |
| Cold-working | O | Oil-hardening |
| | A | Air-hardening; medium alloy |
| | D | High carbon; high chromium |
| Shock resisting | S | |
| High speed | T | Tungsten base |
| | M | Molybdenum base |
| Hot-working | H | H1–H19: chromium base<br>H20–H39: tungsten base<br>H40–H59: molybdenum base |
| Plastic mold | P | |
| Special purpose | L | Low alloy |
| | F | Carbon tungsten |

#### 5.3.1 W-Grade Tool Steels

W-grade steel is essentially high carbon plain-carbon steel. This group of tool steel gets its name from its defining property of having to be water quenched because of its relatively low hardenability. W-group of tool steel is the most commonly used tool steel because of its low cost compared to others. They work well for small parts and applications where high temperatures are not encountered; above 150 °C (302 °F) it begins to soften to a noticeable degree. These steels

can attain high hardness (above HRC 66) and are rather brittle compared to other tool steels. Warping and cracking are very common features of this group of steel. The toughness of W-group tool steels is increased by alloying with manganese, silicon and molybdenum. Up to 0.20% of vanadium is used to retain fine grain sizes during heat treating. Typical applications for various carbon compositions are for W-steels:

a) 0.60–0.75% carbon: machine parts, chisels, setscrews; properties include medium hardness with good toughness and shock resistance.
b) 0.76–0.90% carbon: forging dies, hammers and sledges.
c) 0.91–1.10% carbon: general purpose tooling applications that require a good balance of wear resistance and toughness, such as rasps, drills, cutters and shear blades.
d) 1.11–1.30% carbon: files, small drills, lathe tools, razor blades and other light-duty applications where more wear resistance is required without great toughness. Steel of about 0.8% C gets as hard as steel with more carbon, but the free iron carbide particles in 1% or 1.25% carbon steel make it hold an edge better. However, the fine edge probably rusts off faster than it wears off, if it is used to cut acidic or salty materials.

### 5.3.2 Cold Work Grade Tool Steel

The cold-work tool steels include the O series (oil-hardening), the A series (air-hardening) and the D series (high carbon-chromium). These are steels used to cut or form materials that are at low temperatures. This group possesses high hardenability and wear resistance and average toughness and heat softening resistance. They are used in production of larger parts or parts that require minimal distortion during hardening. The use of oil quenching and air-hardening helps reduce distortion, avoiding the higher stresses caused by the quicker water quenching. More alloying elements are used in these steels, as compared to the water-hardening class. These alloys increase the steels' hardenability, and thus require a less severe quenching process and as a result are less likely to crack. They have high surface hardness and are often used to make knife blades. The machinability of the oil hardening grades is high but for the high carbon-chromium types is low. Some common chemical compositions of O, A and D series along with their applications are given below.

**5.3.2.1 O Series**: 0.90-1.45% C, 1.0–2.0% Mn, 0.3-1.0%Si, 0.3-0.50% Cr, 0-0.3%Mo, 0.0.2%V, 0- 0.50% W. They are used for gauges, cutting tools, woodworking tools to cams, bushings, sleeves, forming rolls, shear blades, etc depending on alloying elements and their contents. All steels in this group are typically hardened at 800°C, oil quenched, then tempered at <200°C.

**5.3.2.2 A Series**: 1.0-1.25% C, 0.5-2.5.0% Mn, 1.0-5.0% Cr, 0.3% Ni, 0.9-1.4% Mo, 0.15–1.4% V. Steels of this series are commonly used for making variety of dies as trimming dies, thread rolling dies and injection molding dies.

**5.3.2.3 D Series:** 1.5% C, 11.0–13.0% Cr; additionally 0.45% Mn, 0.030% P, 0.030% S, 1.0% V, 0.9% Mo, 0.30% Si. These steels retain their hardness up to a temperature of 425°C. Common applications for these tool steels include forging dies, die-casting die blocks and drawing dies. Due to their high chromium content, certain D-type tool steels are often considered stainless or semi-stainless, however their corrosion resistance is very limited due to the precipitation of the majority of their chromium and carbon constituents as carbides because of very high level of carbon content.

### 5.3.3 Shock-resisting Group

The high shock resistance and good hardenability are provided by chromium-tungsten, silicon-molybdenum, silicon-manganese alloying. Shock-resisting group tool steels (S) are designed to resist shock at both low and high temperatures. A low carbon content is required for the necessary toughness (approximately 0.5% carbon). Carbide-forming alloys provide the necessary abrasion resistance, hardenability and hot-work characteristics. This family of steels displays very high impact toughness and relatively low abrasion resistance and can attain relatively high hardness (HRC 58/60). In the US, toughness usually derives from 1 to 2% silicon and 0.5–1% molybdenum content. In Europe, shock steels often contain 0.5–0.6% carbon and around 3% nickel. A range of 1.75% to 2.75% nickel is in Sweden in some shock resisting and high strength low alloy steels (Swedish saw steel).

**5.3.4 High Speed Steel:** It is commonly used as as cutting tool material in power-saw blades and drill bits. It is superior to the older high-carbon steel tools used extensively through the 1940s in that it can withstand higher temperatures without losing its temper (hardness). This property allows HSS to cut faster than high carbon steel, hence the name high-speed steel. At room temperature, in their generally recommended heat treatment, HSS grades display high hardness (above HRC60) and abrasion resistance (generally linked to tungsten and vanadium content often used in HSS) compared with common carbon and tool steels.

High speed steels are alloys that gain their properties from either tungsten or molybdenum, often with a combination of the two. They belong to the Fe–C–X multi-component alloy system where X represents chromium, tungsten, molybdenum, vanadium, or cobalt. Generally, the X component is present in excess of 7%, along with more than 0.60% carbon. The alloying element percentages do not alone bestow the hardness-retaining properties; they also require appropriate high-temperature heat treatment to become true HSS. The addition of about 10% of tungsten and molybdenum in total maximises efficiently the hardness and toughness of high speed steels and maintains those properties at the high temperatures generated when cutting metals. Various series of this group of steel are shown in Table 6.2.

Table 5.2: Various series of high speed steel group.

| Grade | C | Cr | Mo | W | V | Co | Mn | Si |
|---|---|---|---|---|---|---|---|---|
| **T1** | 0.65–0.80 | 4.00 | - | 18 | 1 | - | 0.1–0.4 | 0.2–0.4 |
| **M1** | 0.80 | 4 | 8 | 1.5 | 1.0 | - | - | - |
| **M2** | 0.85 | 4 | 5 | 6.0 | 2.0 | - | - | - |
| **M7** | 1.00 | 4 | 8.75 | 1.75 | 2.0 | - | - | - |
| **M35** | 0.92 | 4.3 | 5 | 6.4 | 1.8 | 5 | - | 0.35 |
| **M42** | 1.10 | 3.75 | 9.5 | 1.5 | 1.15 | 8.0 | - | - |
| **M50** | 0.85 | 4 | 4.25 | .10 | 1.0 | - | - | - |

The original HSS grade tool T1 has been generally superseded by M2. M1 lacks some of the red-hardness properties of M2, but is less susceptible to shock and will flex more. M2 is the "standard" and most widely used industrial HSS. It has small and evenly distributed carbides giving high wear resistance, though its decarburization sensitivity is a little bit high. After heat treatment, its hardness is the same as T1, but its bending strength can reach 4700 MPa, and its toughness and thermo-plasticity are higher than T1 by 50%. It is usually used to manufacture a variety of tools, such as drill bits, taps and reamers. M7 is used for making heavier construction drills where flexibility and extended drill life are equally important. M50 does not have the red-hardness of other grades of tungsten HSS, but is very good for drills where breakage is a problem due to flexing the drill. It is also used in high-temperature ball bearings. The addition of cobalt increases heat resistance and can give a Rockwell hardness up to 67 Min. M35 which also known as Cobalt Steel, HSSE or HSS-E is very similar to M2. It will cut faster and last longer than M2. M42 is a molybdenum-series high-speed steel alloy with an additional 8% or 10% cobalt. It is widely used in metal manufacturing industries because of its superior red-hardness as compared to more conventional high-speed steels, allowing for shorter cycle times in production environments due to higher cutting speeds or from the increase in time between tool changes. M42 is also less prone to chipping when used for interrupted cuts and costs less when compared to the same tool made of carbide. Tools made from cobalt-bearing high speed steels can often be identified by the letters HSS-Co.

### 5.3.5 Hot Working Steels

Hot working steels are a group of steel used to cut or shape material at high temperatures. H-group tool steels were developed for strength and hardness during prolonged exposure to elevated temperatures. These tool steels are low carbon and moderate to high alloy that provide good hot hardness and toughness and fair wear resistance due to a substantial amount of carbide. H1 to H19 are based on a chromium content of 5%; H20 to H39 are based on a tungsten content of 9-18% and a chromium content of 3–4%; H40 to H59 are molybdenum based.

### 5.3.6 P Type tool Steel

P type tool steel is basically for plastic mold steels. They are designed to meet the requirements of zinc die casting and plastic injection molding dies. L-type tool steel is for low alloy special purpose tool steel. L6 is extremely tough. F-type tool steel is water hardened and substantially more wear resistant than W-type tool steel.

## 5.4 Manufacturing of Tool Steels

Tool steels are prepared using various processes such as steelmaking and casting, powder metallurgy (P/M) and the spray process. Here P/M process will not be discussed.

### 5.4.1 Steelmaking

Tool steels are processed through an electrical arc furnace (EAF); secondary refining processes have been introduced recently such as argon-oxygen decarburization (AOD), vacuum-oxygen decarburization (VOD) and the use of ladle furnaces. The principle benefits associated with secondary refining are reduced furnace time, increased overall capacity, improved yield quality, consistency and reproducibility. Most tool steels are processed using EAFs. The cleanliness of the liquid steel and the control of the chemistry are performed in ladle furnace, the AOD process and vacuum arc degassing process (VAD). In the latter process, optimum temperatures for vacuum degassing, refining, as well as final alloy composition and subsequent ingot teeming can be accurately controlled. In addition, stirring the argon under vacuum provides melt uniformity and maximizes the removal of undesirable gases and nonmetallic inclusions from the steel. Next to vacuum arc melting, the VAD process improves cleanliness and hence, mechanical properties in the final product. This process is required when higher levels of polish ability and improving toughness of tool steels are required. If more cleanliness and improved properties are required, vacuum arc remelting (VAR) is employed. In this process, the molten steel from the VAD is teemed into a cylindrical ingot. The ingot is then remelted under vacuum into a water cooled copper mould. The resultant VAR ingot is forged into inter mediate billets or to the final product. To improve cleanliness by reducing nonmetallic inclusions of the steel and to reduce segregation of other processes such as electro slag remelting, P/M and spray forming are used. Electroslag remelting (ESR), which is employed in the production of a relatively small percent age of tool steels, involves passing an electrical current through a consumable electrode of similar chemistry as that desired in the final ingot that resistance melts under a protective, refining slag and is then solidified into an ingot. The electrode is usually of the similar chemistry as the final ingot. The cleanliness of ESR melted product is superior to that of air melted EAF product due to the reduction of sulfur and the removal of inclusions by the ESR, which results in better properties such as fatigue resistance, as illustrated in the Fig.5.6 below.

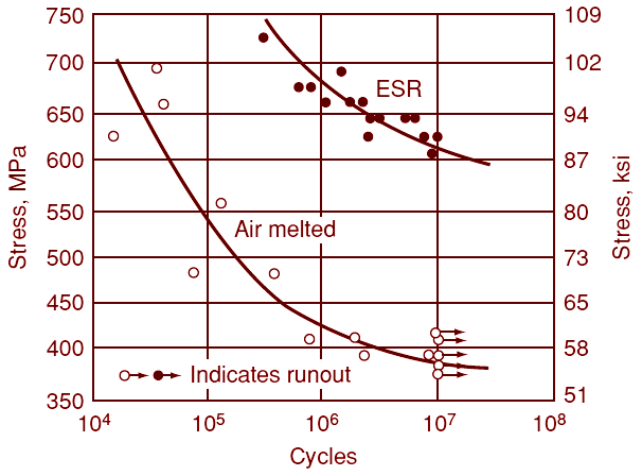



Figure 5.6: Fatigue behaviours of various tool

It is now a major manufacturing process for various types of tool steels such as cold work and hot work tool steels. The powder process involves melting the steel to the desired chemistry and then producing the powder by impinging a thin stream of molten steel with jets of water or gas. The powder is then processed through a series of operations as drying, screening, sintering etc.

**5.5 Heat Treatment of Tool Steels**

The cutting power of tools depends on its hardness, whereas the hardness depends on type of carbides, Fig.5.7. These two properties depend strongly on heat treatment processing and chemical compositions. The heat treatment of tool steels consists of three general stages as (1) heating the steel to form austenite, (2) cooling the steel from austenite to get martensite and (3) tempering to customize required properties. Only difference is that all steps are needed to be controlled very carefully to achieve right form of carbides and their roper volume fraction.

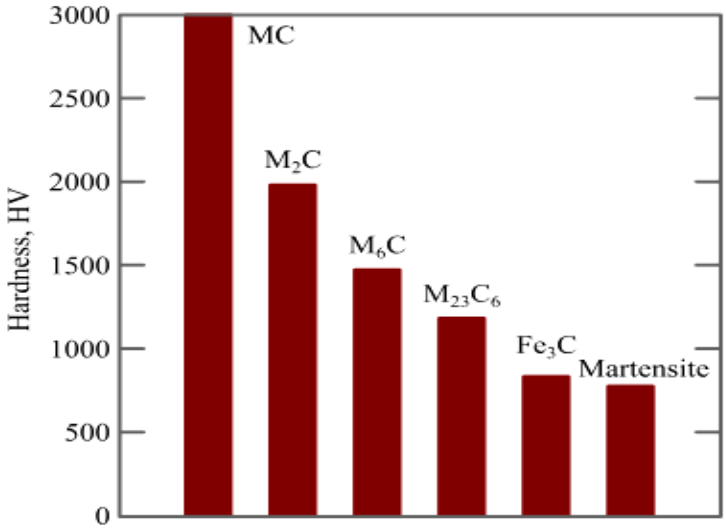



Figure 5.7: Hardness of various carbides.

Figure 5.7 reveals the importance of carbide particles to control hardness of tool steels. Here it is also clear why carbon steel tools are not suitable for heavy duty cutting works. The hardness of this steel is mainly due to martensite and iron carbide, which might be 4-5 time lower than that

of alloy carbides. The schematic diagrams of heat treatment steps required for producing tool steels are in the following Figs.5.8.

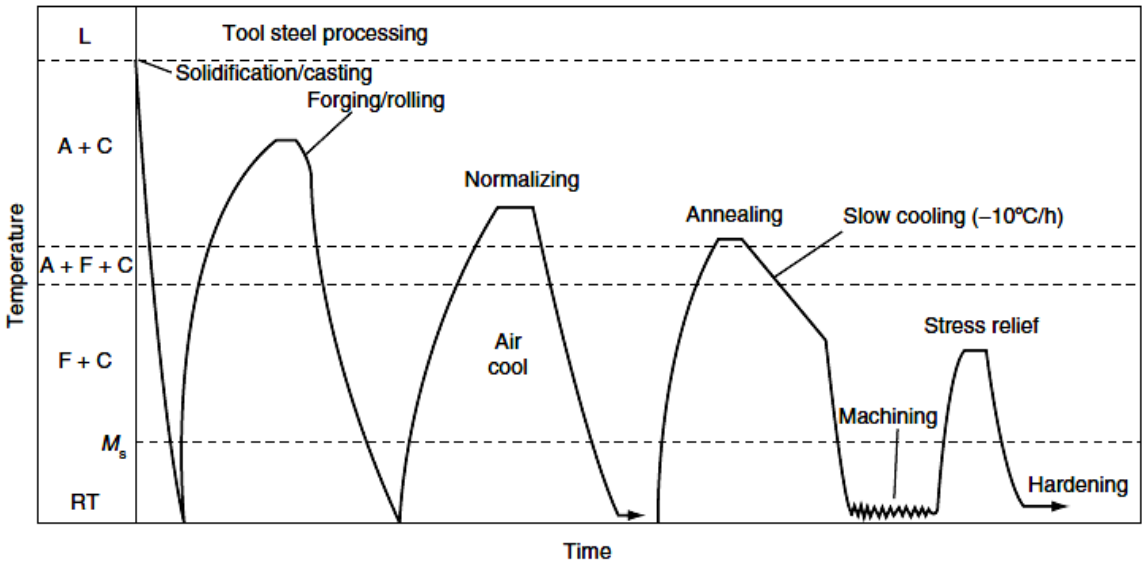



Figure 5.8: Heat treatment cycles for a typical tool steel.

After casting or powder manufacturing and hot working, heat treatment processing steps include normalizing, annealing, machining and stress relief followed by hardening. The final shaping of tool steels by forming and machining is performed before the final hardening heat treatment step, due to the very high as heat treated hardness that makes tool steels very difficult to shape. However, final dimensions can be adjusted by grinding with highly abrasive materials or by electro discharge machining.

Two aspects are of importance to tool steels; the first is homogenization or reduction of microstructure heterogeneity that is produced by segregation phenomenon during solidification and the second is the refinement of grains, which improves the required mechanical properties. Annealing to homogenize the microstructure is based on diffusion phenomenon. This heat treatment consists of maintaining the tool steel at a given temperature for a period of time followed by a controlled cooling rate. A coarse grain size may result from this. The homogenizing treatment is followed by a grain refinement step. This treatment is carried out at a temperature 50$^{o}$C above $Ac_3$ for hypoeutectic steels and above $Ac_1$ for hypereutectic steels. This cycle consists of reheating the steel at the required temperature for a minimum period of time required, followed by cooling in a manner to prevent the formation of bainite. The heat treatment of tool steels is implemented to achieve one of the following:

1. To obtain a desired microstructure and properties suitable for machining or cold deformation
2. To release residual stresses accumulated during previous thermal and mechanical treatments

3. To homogenize the microstructure with globular carbides by a spheroidization treatment

4. To dissolve by a normalizing treatment the intergranular carbides that are detrimental to the mechanical properties of tool steels.

### 5.5.1 Normalizing

Normalizing is a heat treatment that is performed in hot forged or hot rolled tool steels to produce more uniform, fine grained microstructures for subsequent annealing and hardening heat treatments. The normalizing treatment helps to produce a more uniform distribution of precipitates. In tool steels with more stable carbides such as Cr and W carbides, the precipitates may be preferentially aligned in the hot working direction or present at grain boundaries. The normalizing process consists of heating the steel to the temperature region indicated in the Fig.5.9 below.

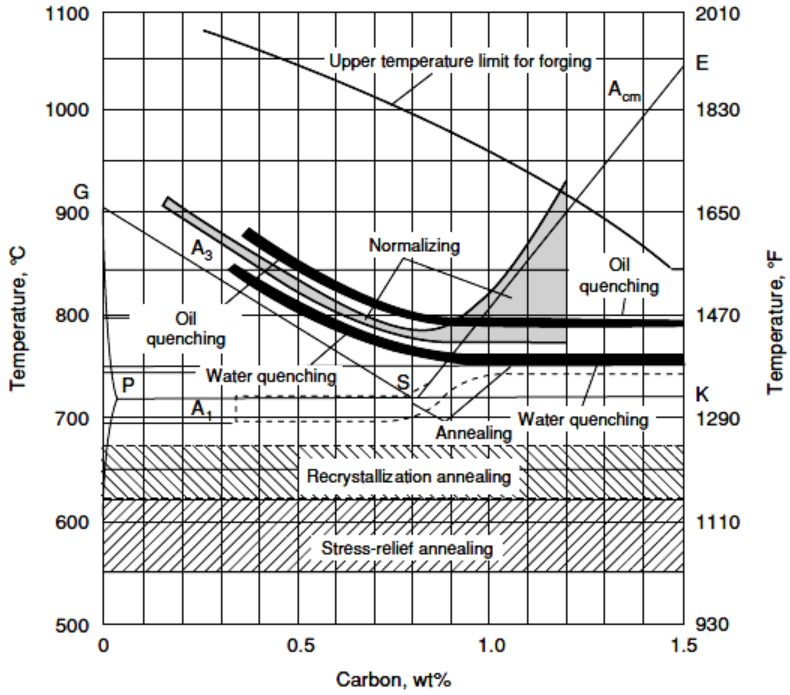



Figure 5.9: Selection of normalizing temperature for tool steel.

During heating and holding at the normalizing temperature, the initial ferrite carbide structure that is stable at low temperatures transforms to austenite. The dissolution of carbides during heating depends on the alloy content of the tool steels. During cooling austenite transforms to ferrite and cementite. In the case of the low alloy tool steels, cementite and pearlite will form during air cooling. The carbides in this structure will be spheroidized in subsequent annealing treatments. In high alloy tool steels, due to their high hardenability, martensite may form during air cooling, which may cause cracking and thus, a normalizing treatment should be avoided for these tool steel grades. Following Tables 5.3 and 5.4 list normalizing and annealing temperatures for different tool steel grades. As previously indicated, high alloy steels should not be normalized.

Table 5.3 Normalizing temperatures of various tool steels.

| Type | Normalizing Temperature, °C | Annealing | | |
|---|---|---|---|---|
| | | Temperature, °C | Rate of Cooling, °C/h | Hardness, HB |
| *Molybdenum high-speed steels* | | | | |
| M1, M10 | Do not normalize | 815–870 | 22 | 207–235 |
| M2 | Do not normalize | 870–900 | 22 | 212–241 |
| M3, M4 | Do not normalize | 870–900 | 22 | 223–255 |
| M7 | Do not normalize | 815–870 | 22 | 217–255 |
| M30, M33, M34, M35, M36, M41, M42, M46, M47 | Do not normalize | 870–900 | 22 | 235–269 |
| M43 | Do not normalize | 870–900 | 22 | 248–269 |
| M44 | Do not normalize | 870–900 | 22 | 248–293 |
| M48 | Do not normalize | 870–900 | 22 | 285–311 |
| M62 | Do not normalize | 870–900 | 22 | 262–285 |
| *Tungsten high-speed steels* | | | | |
| T1 | Do not normalize | 870–900 | | 217–255 |
| T2 | Do not normalize | 870–900 | | 223–255 |
| T4 | Do not normalize | 870–900 | | 229–269 |
| T5 | Do not normalize | 870–900 | | 235–277 |
| T6 | Do not normalize | 870–900 | | 248–293 |
| T8 | Do not normalize | 870–900 | | 229–255 |
| T15 | Do not normalize | 870–900 | | 241–277 |
| *Intermediate high-speed steels* | | | | |
| M50 | Do not normalize | 830–845 | 22 | 197–235 |
| M52 | Do not normalize | 830–845 | 22 | 197–235 |
| *Chromium hot-work steels* | | | | |
| H10, H11, H12, H13 | Do not normalize | 845–900 | 22 | 192–229 |
| H14 | Do not normalize | 870–900 | 22 | 207–235 |
| H19 | Do not normalize | 870–900 | 22 | 207–241 |

Table 5.4 Normalizing temperatures of various tool steels.

| Type | Normalizing Temperature, °C | Annealing Temperature, °C | Annealing Rate of Cooling, °C/h | Annealing Hardness, HB |
|---|---|---|---|---|
| *Oil-hardening cold-work steels* | | | | |
| O1 | 870 | 760–790 | 22 | 183–212 |
| O2 | 845 | 745–775 | 22 | 183–212 |
| O6 | 870 | 765–790 | 11 | 183–217 |
| O7 | 900 | 790–815 | 22 | 192–217 |
| *Shock-resisting steels* | | | | |
| S1 | Do not normalize | 790–815 | 22 | 183–229 (c) |
| S2 | Do not normalize | 760–790 | 22 | 192–217 |
| S5 | Do not normalize | 775–800 | 14 | 192–229 |
| S7 | Do not normalize | 815–845 | 14 | 187–223 |
| *Mold steels* | | | | |
| P2 | Not required | 730–815 | 22 | 103–123 |
| P3 | Not required | 730–815 | 22 | 109–137 |
| P4 | Do not normalize | 870–900 | 14 | 116–128 |
| P5 | Not required | 845–870 | 22 | 105–116 |
| P6 | Not required | 845 | 8 | 183–217 |
| P20 | 900 | 760–790 | 22 | 149–179 |
| P21 | 900 | Do not anneal | | |
| *Low-alloy special-purpose steels* | | | | |
| L2 | 871–900 | 760–790 | 22 | 163–197 |
| L3 | 900 | 790–815 | 22 | 174–201 |
| L6 | 870 | 760–790 | 22 | 183–212 |
| *Carbon–tungsten special-purpose steels* | | | | |
| F1 | 900 | 760–800 | 22 | 183–207 |
| F2 | 900 | 790–815 | 22 | 207–235 |
| *Water-hardened steels* | | | | |
| W1, W2 | 790–925 (d) | 740–790 (e) | 22 | 156–201 |
| W5 | 870–925 | 760–790 | 22 | 163–201 |
| *Tungsten hot-work steels* | | | | |
| H21, H22, H25 | Do not normalize | 870–900 | 22 | 207–235 |
| H23 | Do not normalize | 870–900 | | 212–255 |
| H24, H26 | Do not normalize | 870–900 | | 217–241 |
| *Molybdenum hot-work steels* | | | | |
| H41, H43 | | 815–870 | 22 | 207–235 |
| H42 | Do not normalize | 845–900 | 22 | 207–235 |
| *High-carbon, high-chromium cold-work steels* | | | | |
| D2, D3, D4 | Do not normalize | 870–900 | 22 | 217–255 |
| D5 | Do not normalize | 870–900 | 22 | 223–255 |
| D7 | Do not normalize | 870–900 | 22 | 235–262 |
| *Medium-alloy, air-hardening, cold-work steels* | | | | |
| A2 | Do not normalize | 845–870 | 22 | 201–229 |
| A3 | Do not normalize | 845–870 | 22 | 207–229 |
| A4 | Do not normalize | 740–760 | 14 | 200–241 |
| A6 | Do not normalize | 730–745 | 14 | 217–248 |
| A7 | Do not normalize | 870–900 | 14 | 235–262 |
| A8 | Do not normalize | 845–870 | 22 | 192–223 |
| A9 | Do not normalize | 845–870 | 14 | 212–248 |
| A10 | Do not normalize | 765–795 | 8 | 235–269 |

*Continued*

### 5.5.2 Stress Relief Heat Treatments

Heat treatment usually causes residual stresses, quench cracks and distortion. Residual tensile surface stresses may cause cracking during manufacturing or fracture in service, whereas compressive surface stresses are generally beneficial, they prevent cracking during manufacturing and service and hence improve fatigue strength and resistance to stress corrosion cracking. The objective of a stress relief heat treatment is to reduce residual stresses caused by phase transformation during thermomechanical processing, machining or grinding. There is no microstructural change during this process, which should be performed at temperatures below $Ac_1$ as shown in the earlier Fig.5.9. Stress relief is accomplished by a recovery mechanism. The duration of such a treatment is short and is in the range of 1 to 2 h depending on the section thickness. Stress relieving is performed in air furnaces or salt baths. In this process heating and cooling rates are not critical, however, cooling rates should be slow enough ($300^oC$/h maximum) to prevent the introduction of new residual stress.

There are other heat treatments as annealing and spheroidizing, which are very similar to that discussed in the earlier section.

## 5.6 Carbides in Tool Steels

The microstructure of annealed tool steels consists of ferrite and carbides. The nature of these carbides depends on the chemical composition of the steel. As the performance of tools depends on the morphology and volume fraction of carbides, the control of these two parameters is a very tricky game in the case of heat treatment of tool steels. The types of carbides and some of their characteristics are listed below:

### 5.6.1 $M_3C$

The $M_3C$ carbide is rich in Fe, has an orthorhombic crystal structure and as a consequence it is often referred to as $Fe_3C$ or cementite. The cementite carbide is usually forms first in the early stages of tempering owing to the rapid diffusion of C in Fe (interstitial compound) and the low diffusivity of the substitutional alloying elements like Cr, Mo, V, W, etc. This carbide can take into solution very considerable amounts of other alloying elements, in particular Cr can substitute for Fe gradually as the tempering time and/or temperature increases. If any tool steel is austenitized in such a way that all carbides were dissolved in the austenite, on tempering of the quenched steel, the cementite formation will follow the sequence given below:

$$\text{matrix} \rightarrow \varepsilon\text{-}Fe_{2.4}C \rightarrow Fe_3C$$

Cementite is very unstable carbide. If tempering is continued Fe in cementite will be replaced by Cr and Cr-rich carbide starts to form. It is a rod like carbide that usually precipitates at interlath or intralath boundaries, Fig.5.

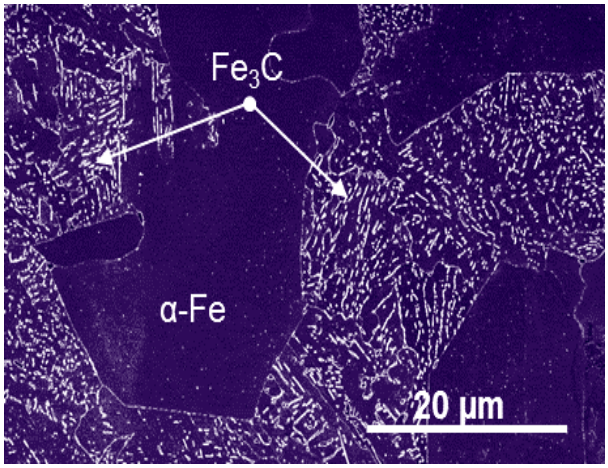



Figure 5.10: $Fe_3C$ carbides in quenched and tempered tool steels.

This is orthorhombic carbide of cementite type, Fig.5.10. M could be iron, manganese or chromium with a minor substitution of W, Mo or V. They are present in low alloy tool steels for cold working applications and in high alloy steels for hot working applications.

### 5.6.2 $M_7C_3$ Carbides

$M_7C_3$ Carbide is a hexagonal type carbide, mostly present in Cr steels. They are resistant to dissolution at high temperature and are hard and abrasion resistant; these carbides are found in tempered high speed steels, Fig.5.11. Typical chemical composition of this carbide is as follows:

C = 8.71%, Cr = 48.35%, Fe = 36.28%

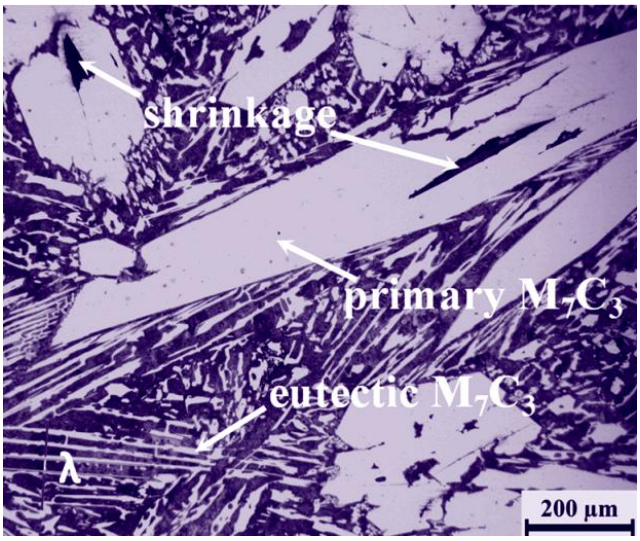



Figure 5.11: Microstructures showing the $M_7C_3$ type carbide in tool steel.

It is a rod and blade shaped carbide. Depending on chemical compositions of the tool steels and tempering time/temperature some other alloying elements may also be present, but they will not be in dominating amount.

### 5.6.3 $M_{23}C_6$ Carbides

$M_{23}C_6$ is a face centered cubic (FCC) type carbides found in high Cr steels and all high speed steels, Fig.5.12. If these steels are kept at high temperature for prolonged time the initially formed carbide $M_7C_3$ a relatively low Cr carbides is replaced by high Cr $M_{23}C_6$ type carbide Here it is to be noted that other elements like W, Mo and V can also be diffused if they are present in the steel. A typical chemical composition of $M_{23}C_6$ carbide is given below.

Cr = 64.0%, Fe = 22.0%, Mn = 7.4%, Mo = 2.6%, V = 2.5%

The tendency of transformation of $M_7C_3$ to $M_{23}C_6$ carbide is very much dependent on the carbon and chromium content, Fig.5.13.

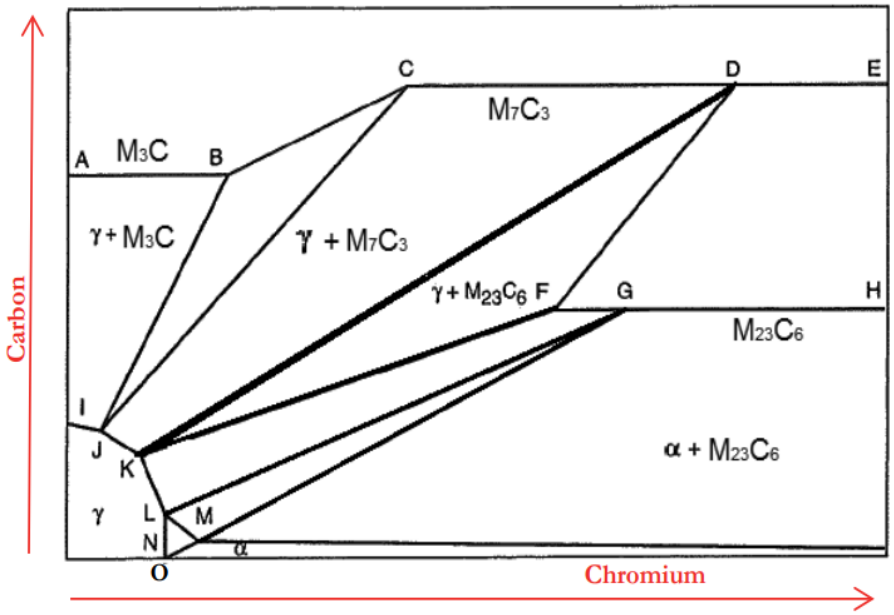



Figure 5.13: Effects of carbon and chromium contents on the Tendency of formation of $M_3C$, $M_7C_3$ and $M_{23}C_6$ carbides in tool steels.

Figure 5.13 clearly indicates that formation of $M_3C$ is only possible in Cr free high carbon steel. It might also form in low Cr content steel if there is very high carbon. Formation of $M_7C_3$ carbide dominates in steels containing high carbon and medium level of Cr. With gradual increase in Cr content $M_{23}C_6$ replaces $M_7C_3$.

### 5.6.4 $M_6C$ and MC Carbides

$M_6C$ is FCC type W or Mo rich carbide (Fig.5.13); may contain some amounts of Cr, V and Co depending on the chemical compositions of the steel present in all high speed steels. They are extremely resistant to abrasion. MC is also FCC type carbide. These carbides are vanadium rich carbides that resist dissolution. The small amount that dissolves plays a role on secondary hardening by reprecipitation. In hypoeutectoid steels and cold working tool steels, the most

favourable annealed structure for machining is pearlite with a fine lamellar structure. In hypereutectoid C steels used for cold working tool steel, the favourable structure for machining is globularized cementite. All alloy steels have a globularized carbide structure in the annealed state. Fine globular carbides uniformly distributed have better properties in service. This is obtained by reducing segregation through appropriate steelmaking practices, large reductions during hot working and appropriate cooling conditions after hot transformation cycles. During the annealing operations, the formation of proeutectoid carbides at grain boundaries should be avoided. These carbides are not soluble during austenitization.

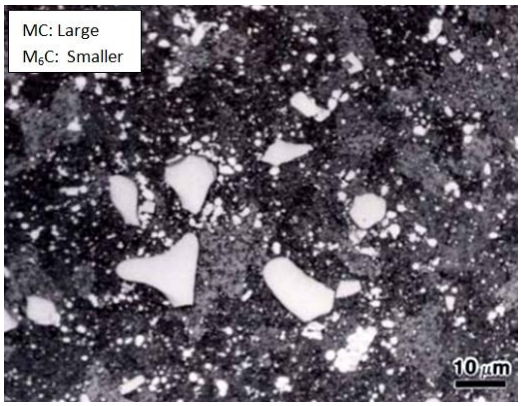



Figure 5.13: Microstructures showing the $M_6C$ and MC type carbides in tool steel.

Finally, it can be concluded that with time and temperature the carbides change their chemico-morphologies depending on relative stability. Unstable carbides, those that will dissociate on heating, can be found at the far left end of each row, Table 5.5.

Table 5.5 Order of stability of various carbides.

| Group-I carbides | Examples | Group-II carbides | Examples |
|---|---|---|---|
| $M_3C$ | $Fe_3C$, $Mn_3C$ | MC | WC, VC, TiC, NbC, ZrC |
| $M_{23}C_6$ | $Cr_{23}C_6$ | $M_2C$ | $Mo_2C$, $W_2C$, $Ta_2C$ |
| $M_7C_3$ | $Cr_7C_3$ | | |
| $M_6C$ | $Fe_3Mo_3C$, $Fe_3W_3C$ | | |

.

## 5.7 Hardening

The hardening operation of tool steels consists of three heat treatment steps: austenitization, quenching to obtain martensite and finally tempering. These steps are discussed below.

### 5.7.1 Austenitizing

The austenitizing heat treatment is the most critical step performed on tool steels. The following precautions have to be observed during austenitizing: to prevent abnormal grain growth, distortion or loss of ductility, excessive carbide dissolution that will affect austenite chemistry and hence hardenability and decarburization that may modify surface chemistry. So, the austenitizing temperature and holding time should be very well controlled. The austenitizing temperature is particularly important for high alloy steels such as high speed steels where the austenitizing temperatures are close to the solidus temperature. We know tool steel is a very complex alloy steel group and that it needs a very close temperature control for heat treatment. So, knowledge on the effects of alloying elements on the eutectic temperature as well as on the eutectoid carbon content is very important. The effects of alloying elements on eutectoid temperature (top) and eutectoid composition (bottom) are given in following Fig.5.14.

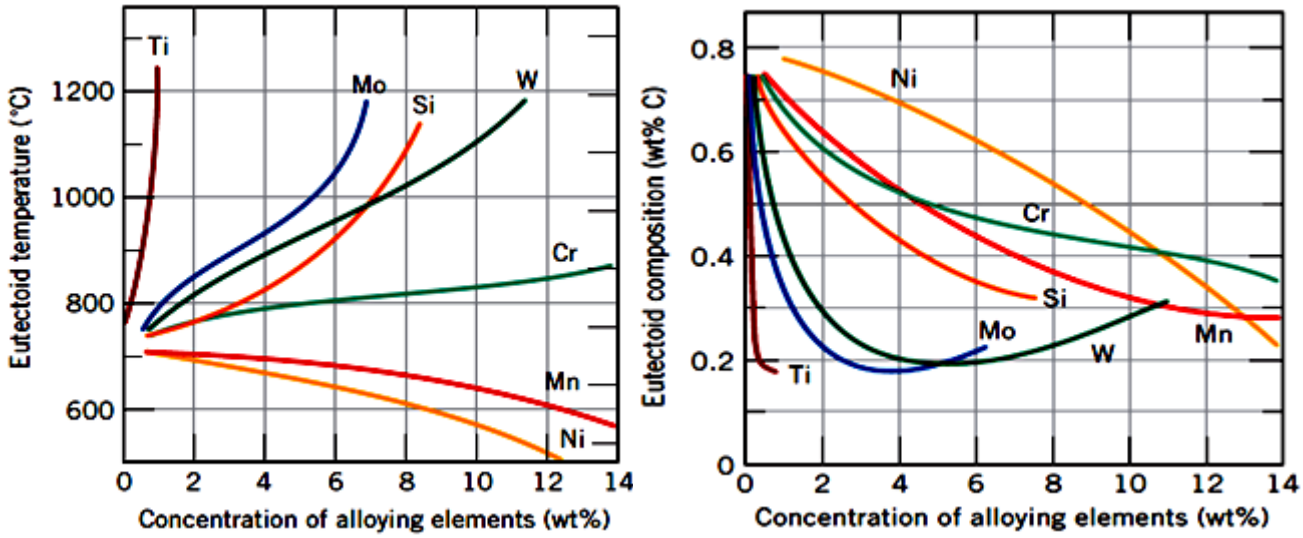



Figure 5.14: Effects of alloying elements on eutectoid temperature (left) and carbon content (right).

Alloying elements used in tool steels are categorized either as ferrite stabilizing elements that reduce austenite phase domain, or austenite stabilizing elements that extend it as shown in the following Table 5.6.

Table 5.6: Ferrite and austenite stabilizing alloying elements.

| Ferrite-Stabilizing Elements | Austenite-Stabilizing Elements |
|---|---|
| Chromium | Carbon |
| Molybdenum | Cobalt |
| Niobium | Copper |
| Silicon | Manganese |
| Tantalum | Nickel |
| Titanium | Nitrogen |
| Tungsten | |
| Vanadium | |
| Zirconium | |

Following Fig.5.15 show the effect of Mn, Cr and Mo on the extent of the phase field of pure austenite at elevated temperature.

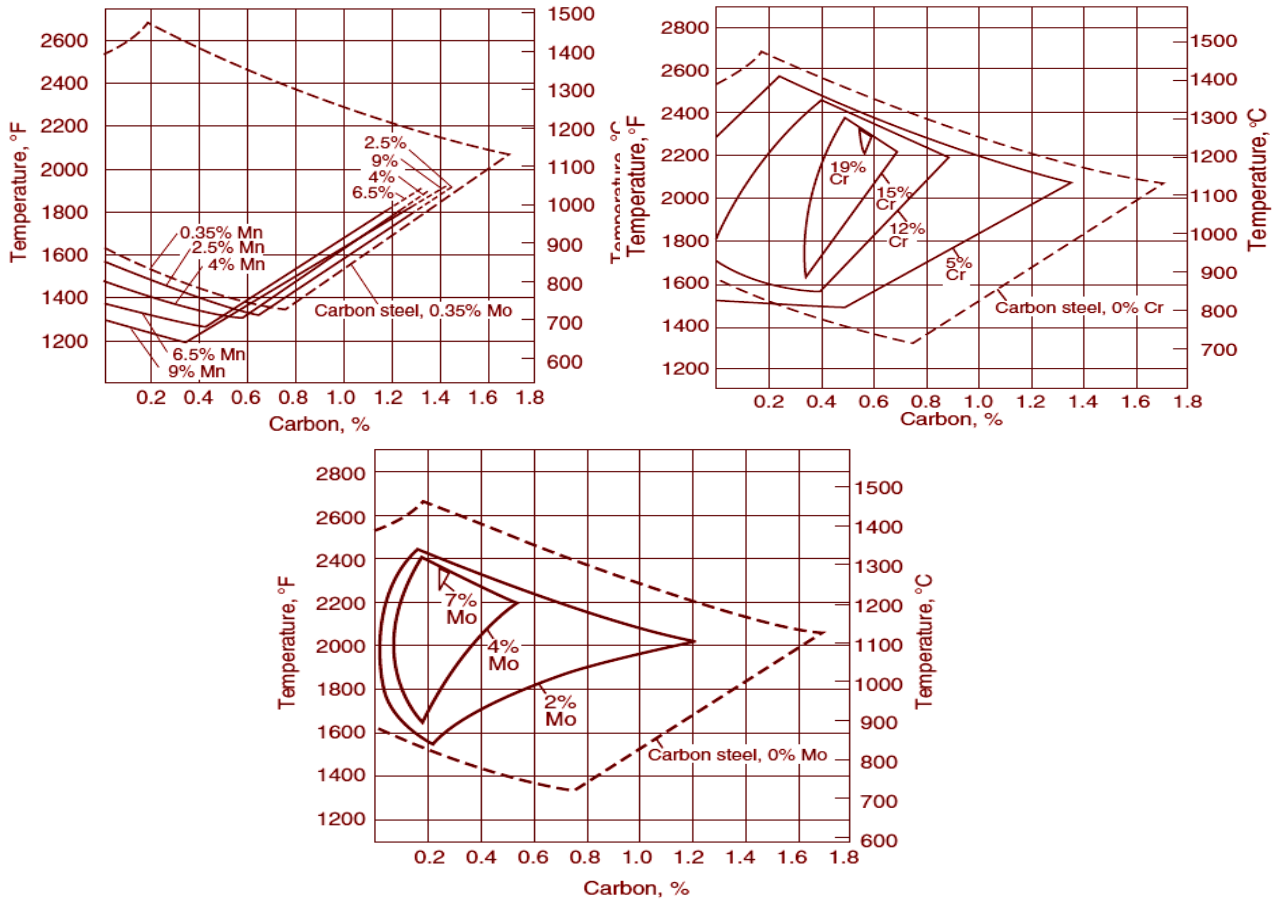



Figure 5.15: Effects of Mn, Cr and Mo contents on austenite phase field of

During reheating in the austenite region, the ferritic structure with carbides transforms into austenite with or without carbides, depending on the chemical composition of the tool steels. In low alloy steel, a homogeneous austenitic microstructure without carbides may form during austenitization treatment. In high alloy tool steels, the resultant microstructure consists of austenite or austenite and carbides that are not dissolved. In ledeburitic steels, not all carbides are dissolved during reheating, even at the liquidus temperature. The microstructure of annealed low alloy tool steels consists of ferrite and $M_3C$ type carbides, which are easily dissolved in the austenite region. Generally, the quenching temperature is 50$^oC$ above $Ac_3$ as mentioned in the earlier section. These temperatures are good to compromise between dissolution of carbides and minimizing austenite grain growth. The austenitizing treatment, 30 min per 25mm thickness of the heat treated tool in the temperature range of 750 to 900$^oC$, is sufficient for homogenization. In highly alloyed steels and ledeburitic steels, the austenitizing temperatures are higher than the low alloy steels, due to the difficulty of dissolution of carbides of the type $M_7C_3$, $M_{23}C_6$, $M_6C$ and MC present in the annealed microstructure. The dissolution of these carbides depends on the annealing temperature, austenitizing temperature and the holding time at this temperature. So,

quenched microstructures of tool steel may contain carbide free martensite or martensite along with undissolved alloy carbides, Fig.5.16.

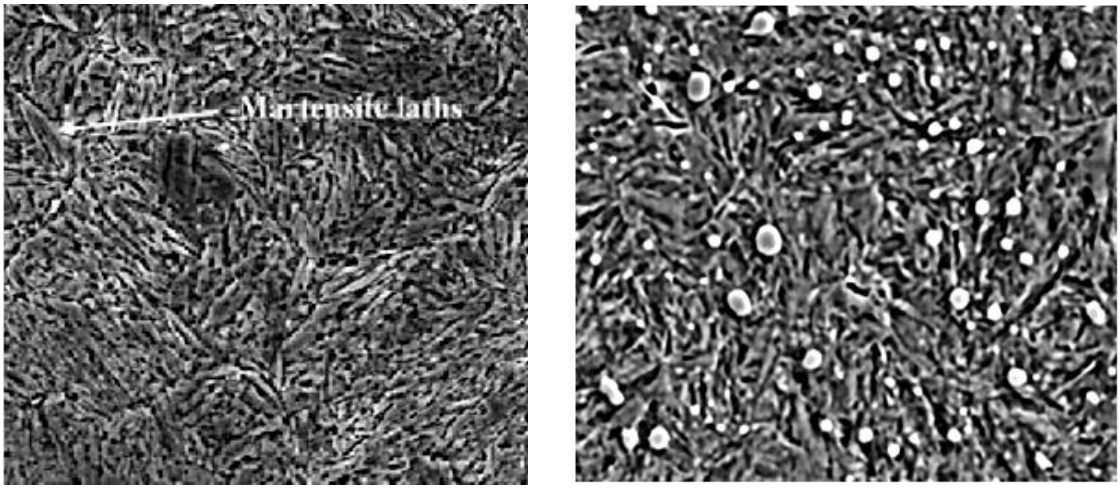



Figure 5.16: As quenched carbide free martensite (left) and martensites with undissolved carbides.

### 5.7.2 Quenching

During quenching from the austenitizing temperature, austenite may transform to martensite with some volume fraction of RA. This is possible when the austenite to ferrite or carbide transformation is suppressed by high cooling rates or alloying elements that retard this transformation. Quenching media are typically water, brine, oil, salt, inert gas or air depending on the composition and the thickness of the tool steel.

#### 5.7.2.1 Retained Austenite in Quenched Steel

After quenching, the microstructure of tool steels consists of martensite and RA. The latter reduces the hardness of the steel and affects the properties of tools in service. During work hardening RA transforms to martensite. The quantity of RA that is related to the reduction of $M_f$ depends on the chemical composition, austenitizing temperature, and cooling rate. RA increases with increasing austenitizing temperature due to the increase of carbon content and other alloying elements by the dissolution of carbides present in the annealed structures. All of the alloying elements, except cobalt, lower $M_s$. Carbon has the most powerful effect on $M_s$ temperature. The higher the alloy contents of austenite, the lower the $M_s$ temperature and the greater the amount of RA at room temperature. For a given tool steel alloy and austenitizing conditions, the content of RA varies with cooling rate and is maximum around the critical cooling rate for marten site.

### 5.7.16. Tempering

Tempering, which is the final step of the heat treatment of tool steels, consists of heating the as quenched microstructure to temperatures below the transformation temperature $Ac_1$. It is a very complex phenomenon originating from the as-quenched microstructure of tool steels, which

consists primarily of martensite with RA and carbides. During tempering there are three to five transformation steps that occur depending, on the alloying of too l steels:

1. In the first step between 50 and 200$^{o}$C, there is precipitation of epsilon carbides, which delays the softening of the as-quenched structure. During this step a volumetric contraction occurs.

2. The second step is between 200 and 350$^{o}$C, during which dissolution of epsilon carbide and precipitation of cementite are occurring along with a reduction in hardness.

3. The temperature range of the third step depends on the chemical composition of the steel and corresponds to a reduction in the stability of RA. This instability is produced by carbide precipitation, which reduces the alloy content in solution in the austenite, the and hence increases $M_s$. This instability starts at 150$^{o}$C and 450$^{o}$C , for carbon steels and high alloy tool steels, respectively. The transformation of RA to martensite or bainite during cooling results in a volume increase. This expansion increases with increasing volume fraction of RA.

4. The fourth stage starts at about 500$^{o}$C and corresponds to highly alloyed tool steels containing carbide forming elements. There is an exchange of carbon between cementite and other carbides; this phenomenon is associated a large volumetric expansion.

5. The fifth stage, which is also associated with highly alloyed tool steels, starts at 600$^{o}$C and continues until $Ac_1$. It corresponds to the coalescence of carbides and results in an annealed microstructure. This phenomenon is associated with a volumetric contraction. It is necessary that the person designing the heat treatment be familiar with the nature of the dilatations that occur during the tempering operations in order to arrive at the proper final dimensions prior to heat treatment. Microstructures of high speed tool steels after this stage of tempering with and without preexisting carbides are shown in Fig.5.17.

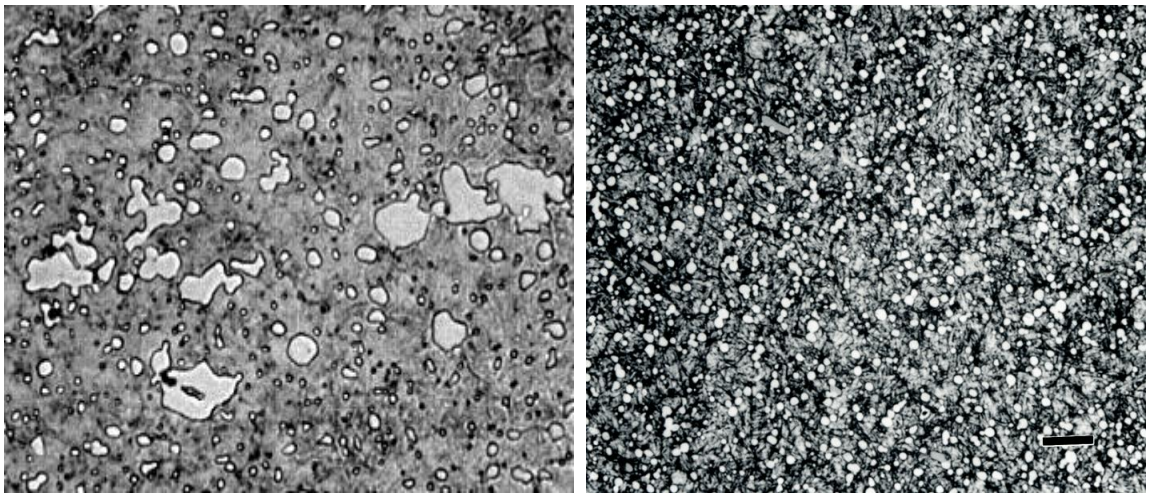


Figure 5.17: Tempered martensites in high speed steels with (left) and without (right) undissolved

The variation of the hardness of tool and die steels with respect to the tempering temperature would have one of the four principal behaviours given in the following Fig.5.18.

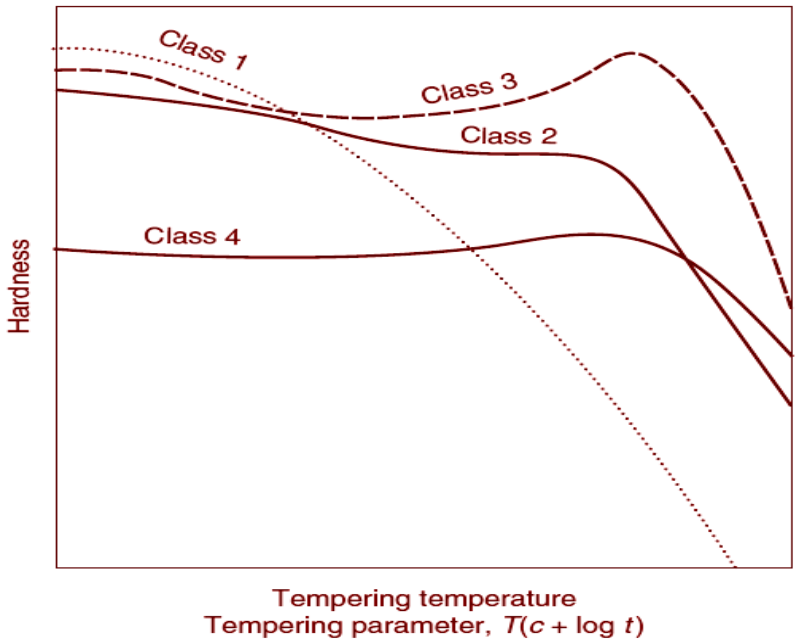



Figure 5.18: Effects of tempering temperature on the hardness of quenched tool steels.

Class 1 is typical of carbon and low alloy tool steels in which the hardness is decreasing progressively with increasing temperature due to the precipitation and coarsening of cementite, or of other low alloy carbides.

Class 2 is characteristic of medium to high alloy cold working die steels in which the alloying addition retard s carbide precipitation and related softening. Curves between Class 1 and Class 2 could be obtained for low to medium alloy steels.

Class 3 is representative of highly alloyed high speed steels in which secondary hardening occurs at high tempering temperatures. The final hardness of these steels could exceed that in the untempered condition.

Class 4 is representative of the medium to high alloy hot working tool steels that exhibit a secondary hardening, as is the case with Class 3. In Class 4, the as quenched hardness is lower than that of class 3 due to its lower carbon content.

Secondary hardening is a result of the transformation of RA to martensite on cooling from the tempering temperature, and of precipitation of an ultrafine dispersion of alloy carbides. Tungsten, vanadium, chromium and molybdenum that are the strong carbide forming elements are most commonly used to achieve secondary hardening. To take advantage of their precipitation characteristics, they must be dissolved in austenite during the austenitizing

treatment in order to be incorporated into the martensite formed during quenching with sufficient super saturation for secondary hardening during tempering. Following Fig.5.18) show the effect of strong carbide forming elements (vanadium, tungsten, molybdenum and chromium) on the secondary hardening of 0.5%C tool steel.

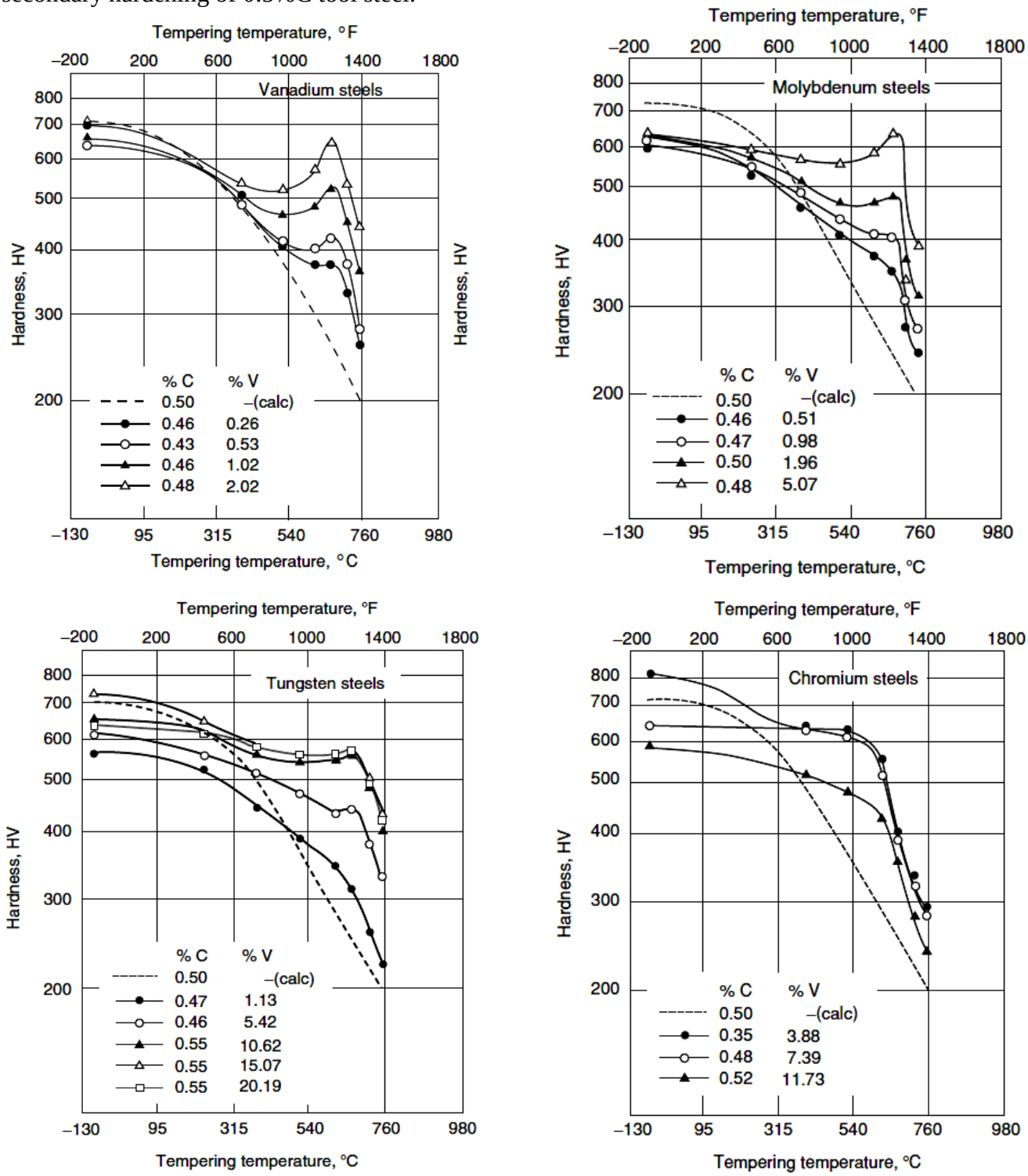



Figure 5.18: Effects of tempering temperatures and vanadium contents on the secondary hardening of various tool steels.

In the case of class III steel, i.e. for high speed steels, tempering up to a certain temperature the overall hardness in the final product increases, Fig.5.19. Here, up to 350$^{o}$C, the hardness of martensite gradually decreases. If the tempering temperature is further increased, then low hardness retained austenite transforms to martensite that contributes to increase in hardness of the tempered martensite. After 500$^{o}$C, very fine precipitation of high alloy carbides starts to forms, which increase the hardness of the matrix very sharply u to temperature around 800$^{o}$C. Then it starts to decrease if tempering temperature is further increased because of coarsening of carbide particles.

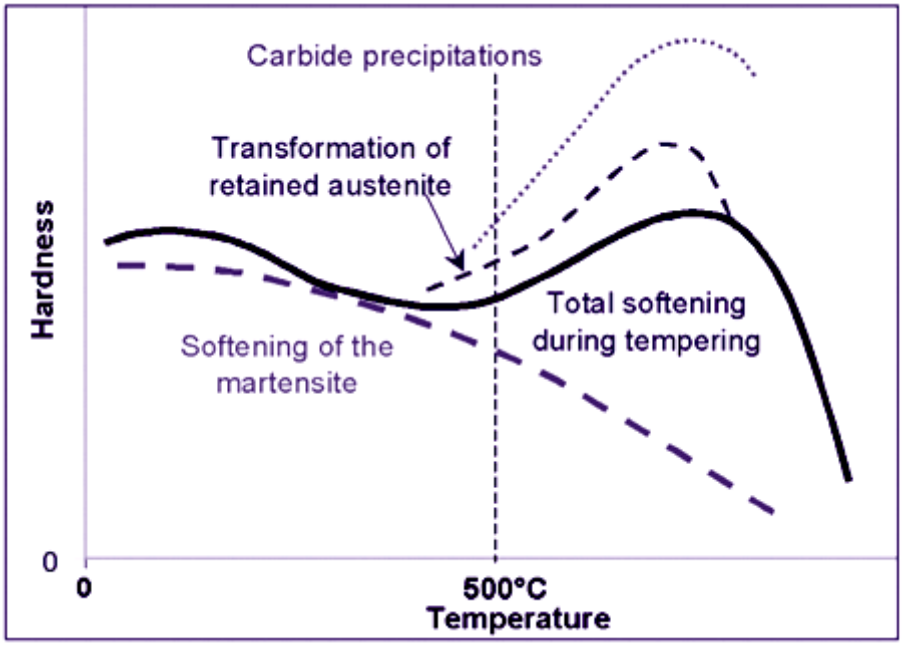



Figure 5.19: Softening and hardening tendency of high speed steel during tempering.

**5.7.3.1How Many Tempers are Required?**

Two tempers are generally recommended for tool steel, except in the cases of large cross sections, parts with complex geometries or very high demands on dimensional stability. In these cases, a third tempering is usually needed, Fig.5.20.

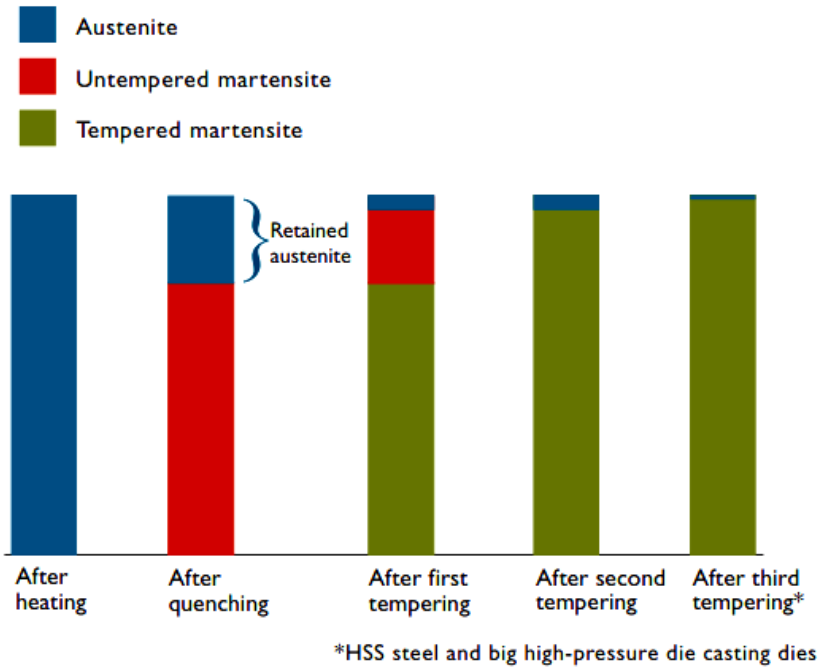



Figure 5.20: Effects of tempering repetitions on retained austenite transformation in tool

It is possible to make use of different combinations of these factors that will result in the same hardness level. Quality heat treatment delivers not only desired hardness but also optimized properties of the material for the chosen application. Tool steels should always be at least double tempered. The second tempering takes care of the newly formed martensite during cooling after the first tempering. Three tempering modes are recommended in the following cases:

a) High speed steel with high carbon content
b) Complex hot work tools, especially in the case of die casting dies
c) Very large moulds for plastic applications
d) When high dimension stability is a demand (such as in the case of gauges or tools for integrated circuits)

It should be noted that tempering at low temperatures only affects the martensite, while tempering at high temperature also affects the retained austenite. After one tempering at a high temperature, usually the microstructure consists of tempered martensite, newly formed martensite, some retained austenite and carbides. Precipitated secondary (newly formed) carbides and newly formed martensite can increase hardness during high temperature tempering. Typical of this is the so called secondary hardening of e.g. high speed steels and high alloyed tool steels. It is very important to have in mind that hardness is the result of several different factors, such as the amount of carbon in the martensitic matrix, the microstresses contained in the material, the amount of retained austenite and the precipitated carbides during tempering.

## 5.8 Some Special Features of HSS

### 5.8.1 Heating of tool Steels for Hardening

High seed steel usually contains higher level of alloying elements, i.e. their carbon equivalent is quite high. In the earlier section, it has been mentioned that steels having carbon equivalent more that 0.7 should be heat treated carefully, where preheating is must. For homogeneity in chemical compositions as well as in microstructures and to avoid any undue cracking and warpage the HSS component must be preheated. The standard heat treatment cycle in this case is shown in Fig.5.19.

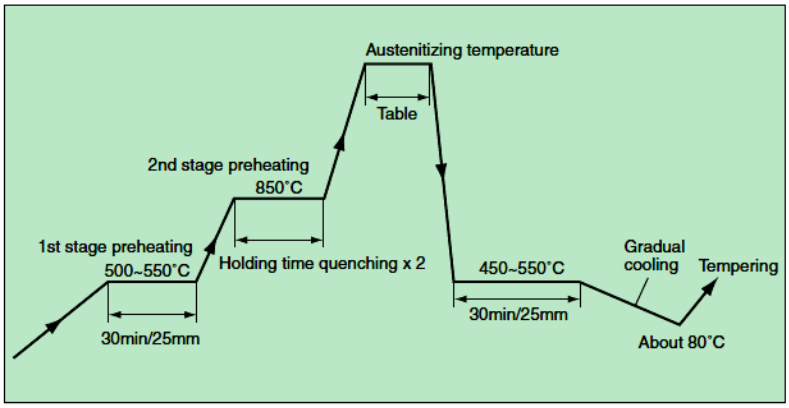



Figure 5.19: The standard heat treatment cycle for HSS steel.

Not only heat treatment cycle and temperature at each level, holding time at each level is very important, which can be calculated using the following Table 5.7

Figure 5.7: Holding time selection for hardening of various HSS.

**Holding time at austenitizing temperature**

| Heating furface | Thickness (mm) / Time | 5 | 10 | 20 | 30 | 40 | 50 | 60 | 70 | 80 | 90 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Salt bath | Holding time (sec) | 60 | 90 | 160 | 240 | 280 | 350 | 390 | 420 | 440 | 495 |
| | Magnification(Holding time/Thickness) | X12 | X9 | X8 | X8 | X7 | X7 | X6.5 | X6 | X5.5 | X5.5 |

### 5.8.2 Relation Between Carbon Concentration and Total Alloy Content

As regards to materials used for profile cutting tools, their most important properties are hardness and resistance to failures in service, e.g., cracking or breaking, which are expressed by their material impact toughness or fracture toughness. Especially the high ductility of the material makes the tool predisposed for work in the impact loads conditions, and also in conditions resulting in fatigue failure. Ensuring these expected service properties is achieved for the material with the particular chemical composition during its heat treatment.

Chemical composition and structure of the contemporary high-speed steels result from decades of experimental research. It is assumed that the first high-speed steel was the one developed in 1900 by F.W. Taylor and M. White, containing 1.85% C, 0.15% Si, 0.3% Mn, 3.8% Cr, and

8.0% W. Work on development of the high-speed steels led to introducing into the steel an addition of vanadium as well as cobalt. The next modification of the high-speed steels chemical composition concerned partial replacement of tungsten with molybdenum. Further experimental research led to the simultaneous concentration increase of vanadium and carbon, and next to reducing the tungsten concentration, increasing vanadium concentration. All that made it possible to develop steels with the high concentration of carbon and vanadium, called the super high-speed steels. Therefore, evolution of the high speed steels composition since their origin until the end of World War II. The main alloying elements in the high-speed steels currently are chromium, tungsten, vanadium, molybdenum and cobalt. Silicon, niobium, and titanium are introduced as alloy additions sometimes apart from the main elements mentioned above.

The high speed steels properties depend significantly on the proportion between the carbon concentration and the alloy equivalent as calculated from the following relationship.

$$\text{Equivalent Alloy} = \%W + 1.9\%Mo + 6.3\%V$$

There is relationship between the equivalent alloy content and equivalent carbon concentration (C), which is given below:

$$C = \frac{\text{Equivalent Alloy Content}}{30}$$

From the point of view of service properties, that the steels with additions of tungsten, molybdenum and vanadium should contain the carbon concentration higher by 0.1- 0.2% than the equivalent carbon concentration. The relationship between carbon concentration and equivalent alloy content is shown in Fig.5.20.

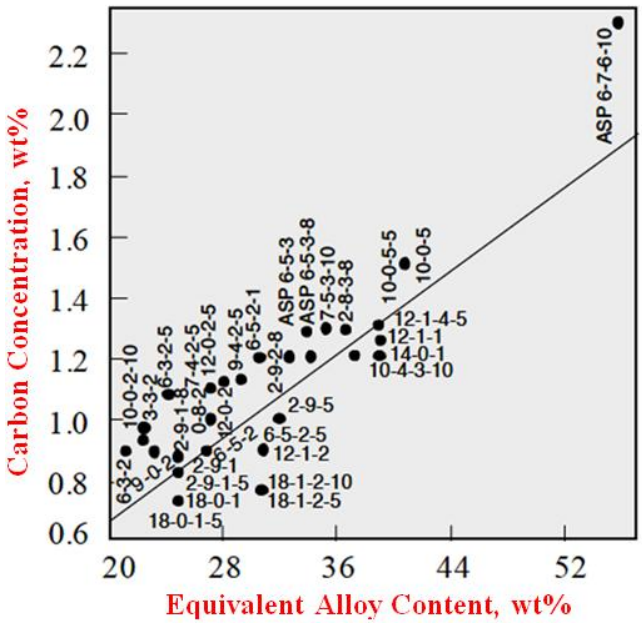


Figure 5.20: Relationship between carbon concentration and equivalent alloy content.

After full ausenitization, the steel needs to be quenched in proper media for optimum roperties. Proper knowledge on the continuous cooling curves of HSS steel is very important to optimimize the matrix microstructures as well as carbide recipitation control. The transformation diagram of a typical HSS (0.90C, 0.30Si, 0.30Mn, 4.10Cr, 5.00Mo, 1.90V and 6.40W) is shown in Fig.5.21.

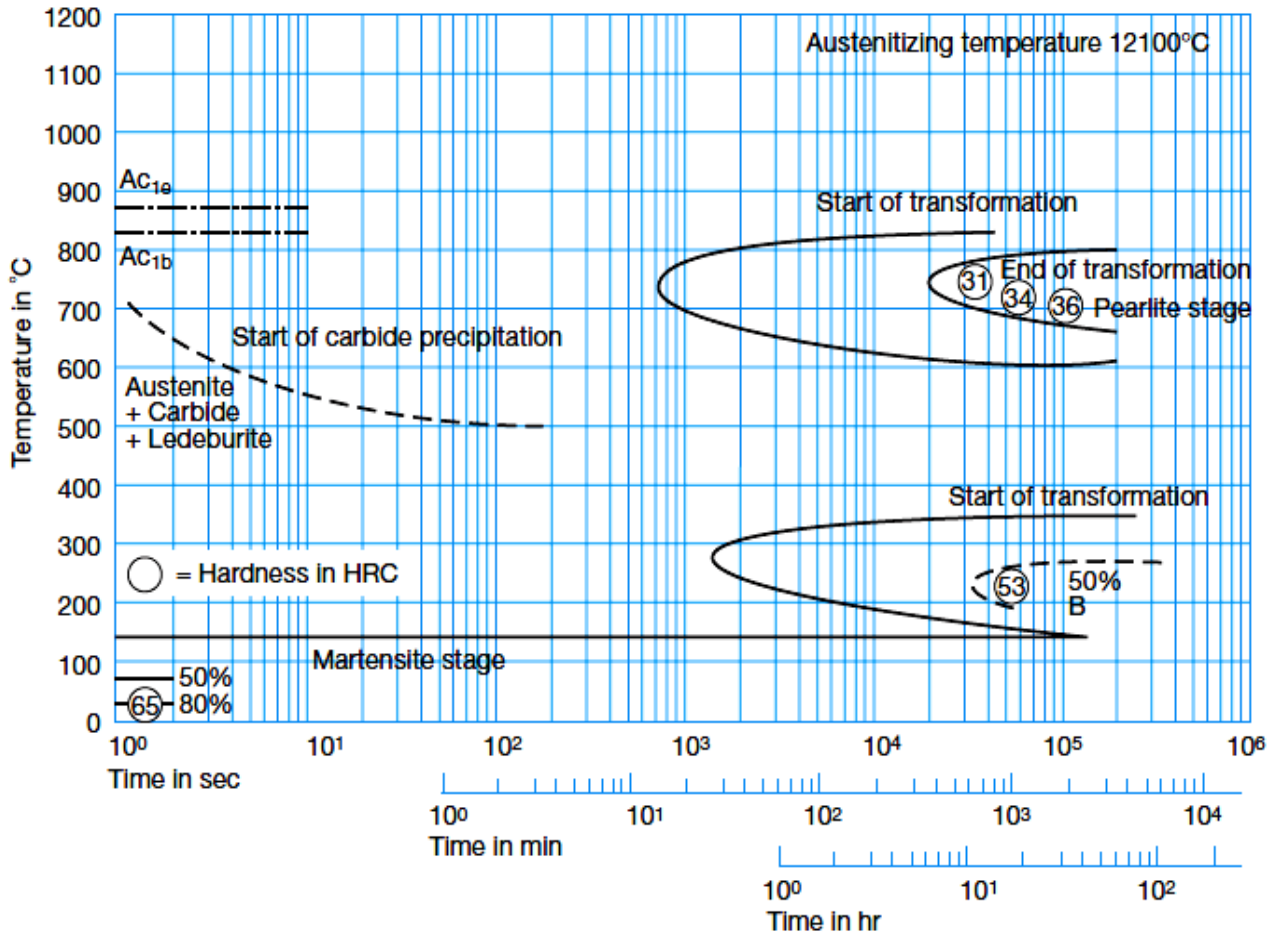



Figure 5.21: Transformation diagram of a typical HSS.

Unlike high carbon or conventional alloy steels, the hardness of the HSS might be increased if it is tempered at proper temperature. Like other steels, HSS softened during the initial stage of temering. Then it starts to recover the lost hardness and then exceeds the vale its hardness of as quenched condition, Fig.5.22. To get otimum level of hardness for a paticular tool steel chemical comositions, similar to transformation diagram, knowledge on the hardness versus tempering temperature diagram is also important. Because, the peak hadness gain temperatures are different for different steels.

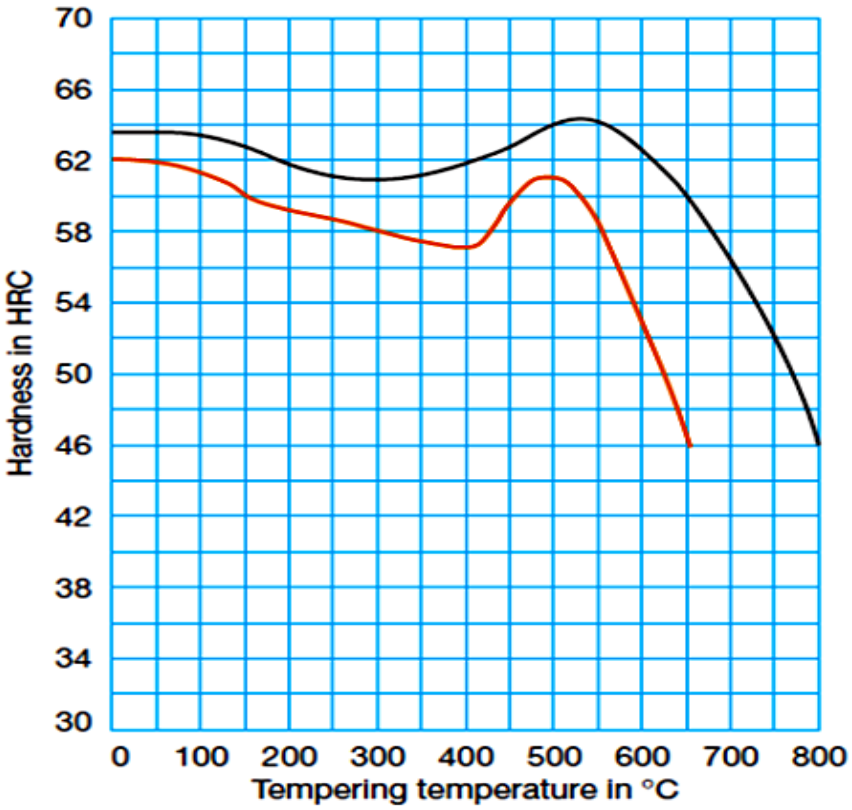



Figure 5.22: Tempering behavours of two different high steed steels.

# Chapter Six

## Heat Treatment of Stainless Steel

### 6.1 Introduction

Stainless steels are frequently classified according to their microstructure into five types: austenitic, ferritic, martensitic, duplex (ferritic-austenitic) and precipitation hardenable (PH). More common types, such as the austenitic, ferritic and martensitic stainless steels, have been discovered in the first decade of the 20th century.

Phase diagrams are important to predict the phases that are present in the stainless steels; therefore, they are also very important as a guide to their heat treatments. However, they do have some limitations due to the complexity of the multicomponent thermodynamic calculations and also due to the transformation kinetics that may prevent the attainment of the equilibrium phases. Regarding the first limitation, the number of relevant components is often more than five and published diagrams are rarely found to contain more than four components. As to the second limitation, the diffusion of alloying elements in the solid state can be very slow, especially in the case of austenitic stainless steels, where the precipitation of certain intermetallic compounds can take thousands of hours.

### 6.2 Equilibrium Diagrams

In this section the most relevant features of the binary diagrams Fe–Cr, Fe–Ni and Fe-Cr–Ni will be discussed. The three main features of the Fe-Cr diagram shown in the Fig.6.1, which are relevant to stainless steels, are the ferrite-stabilizing character of Cr and the presence of sigma (σ) and alpha prime (α’) phases.

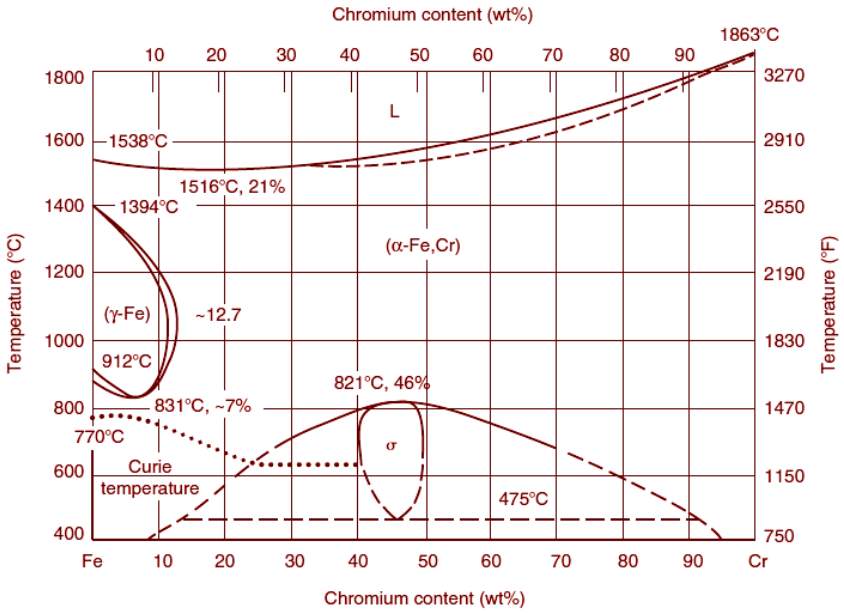



Figure 6.1: Fe-Cr binary phase diagram.

The Fe–Ni diagram shows the strong austenite stabilizing effect of Ni, Fig.6.2. The intermetallic compound $Ni_3Fe$ is not normally observed in stainless steels. Because, to get Fe-Ni intermetallic compound the alloy must contain more than 60%Ni, which is usually not available in the stainless steel.

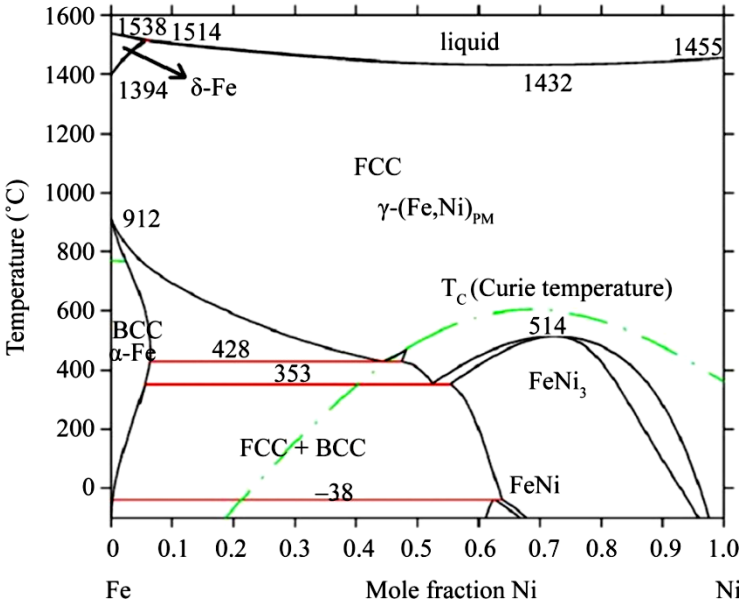



Figure 6.2: Fe-Cr binary phase diagram.

The ternary Fe-Cr-Ni diagram is the basic diagram for stainless steels (Fig.6.3 given below). It shows the presence of only three solid phases: austenite, ferrite and sigma phases. For a high Cr/Ni ratio delta ferrite may occur during solidification and sigma phase may occur during aging at temperatures between 550°(1020°F) and 900°C (1650°F). The compositional range of the sigma-phase field increases as the temperature is below 900°C.

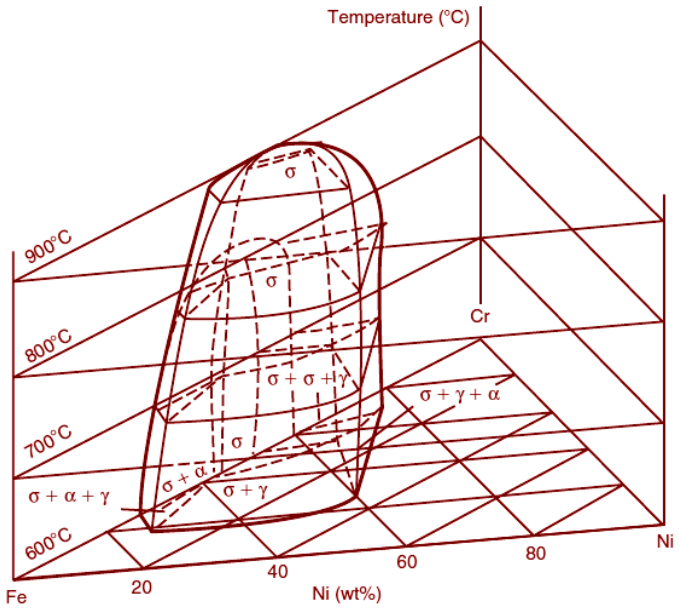



Figure 6.3: Fe-Cr-Ni ternary system.

The Fe–Cr–Mo diagram (Fig.6.4) shows the presence of six phases: (Fe,Cr) = solid solution; (Cr,Mo) = solid solution; $Fe_7Mo_6$ = mu (m) phase; σ = sigma phase; χ = chi phase; the Laves phase η-$Fe_2Mo$.

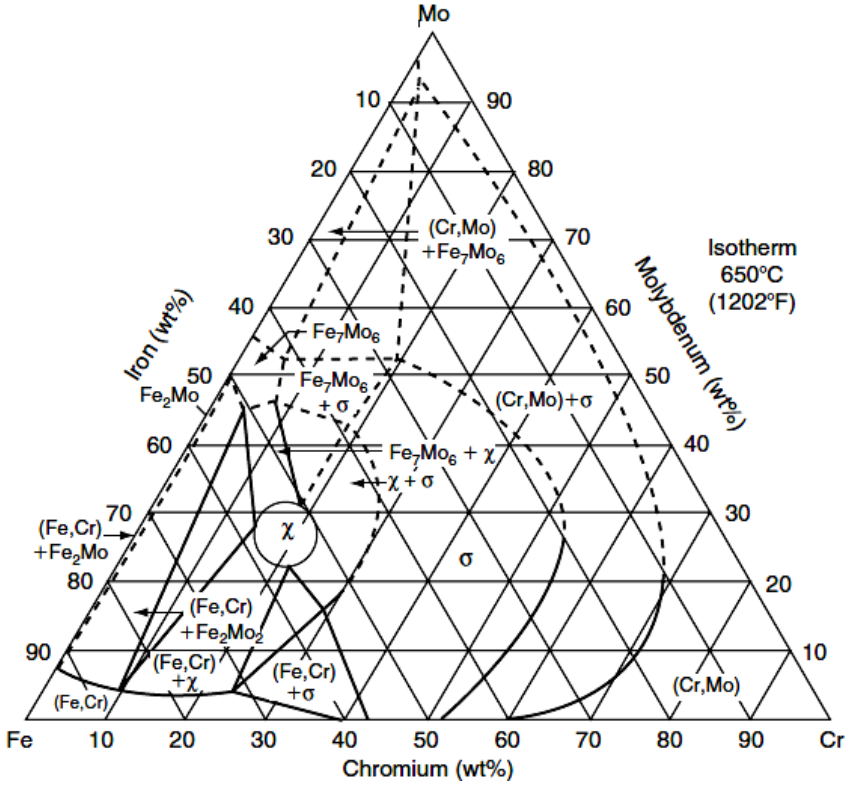



Figure 4: Fe-Cr-Mo equilibrium phase diagram.

Intermetallic phases that occur in stainless steels can be classified into two groups: (i) topologically close packed (TCP) phases, like σ, χ, Laves (η), G, R and Mu (μ) and (ii) geometrically close packed (GCP) phases, like γ', γ'', η-$Ni_3Ti$ and δ-$Ni_3Nb$. TCP phases are characterized by close packed layers of atoms separated from each other by relatively large interatomic distances. The layers of close packed atoms are displaced from one to the other by sandwiched large atoms, developing a characteristic topology. In contrast, the GCP phases are close packed in all directions. GCP phases have been observed to form mainly in nickel base alloys whereas the TCP phases have been observed mainly in the iron base alloys. The other elements like carbon, nitrogen, boron and sulfur are usually present in relatively small quantities but their effect can be extremely important.

Useful equilibrium phase diagrams might be available, however, they are not always sufficient to predict the resulting microstructure after solidification. As a result practical methods were developed. Of these, the best known is the Schaeffler diagram. Schaeffler divided the alloying elements into two groups: ferrite and austenite stabilizers. He also developed a formula by means of which the elements of each group could be expressed as a chromium equivalent and as a nickel equivalent, Fig.6.5.

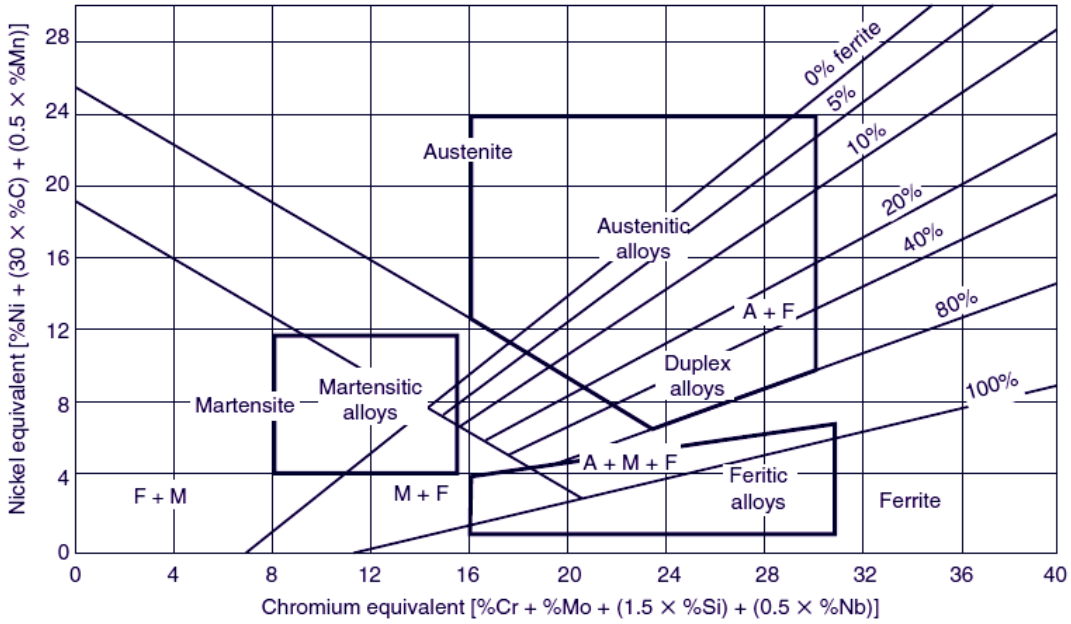



Figure 6.5: Schaeffler's constitution diagram for stainless.

The regions of the diagram represent the microstructures that can be observed for each class of stainless steels. Schaeffler's method, therefore, allows a rough evaluation of the microstructure as a function of the steel composition, however it does not take into consideration the influence of the cooling rate and aging heat treatments. These diagrams have also been used to estimate the microstructure of the weld metal. The empirical formulas and the experiments present a considerable scatter with regard to the determination of the amount of delta ferrite in austenitic weld metal.

### 6.3 Austenitic Stainless Steels and Its Heat Treatment

The discovery of stainless steels could be linked to a significant advance in the development of corrosion and oxidation resistant materials. At the time of their discovery, however, the austenitic stainless steels were frequently susceptible to intergranular corrosion, also called sensitization, caused by chromium depleting in the areas next to grain boundaries, due to the precipitation of the $M_{23}C_6$ carbide. Two approaches have been attempted to solve this problem: reduction of the carbon content (that resulted in the low carbon, or L type, such as the AISI 304L and 316L types) and the addition of alloying elements that had more affinity with carbon as compared to Cr, such as Ti and Nb (that resulted in the stabilized types, such as the AISI 321 and the 347, respectively). Another important alloying modification in the austenitic stainless steels was the addition of Mo aiming at the resistance to pitting corrosion, with additions usually about 2 to 3 wt%, such as the AISI 316 and 316L types, although higher contents, such as 3 to 4 wt%, are present in the AISI 317 and 317L types.

The austenitic stainless steels usually present an excellent combination of corrosion resistance, ductility, toughness and weldability. However, for the common types their strength level,

particularly the YS in the annealed condition, is relatively low, around 200 to 250 MPa. Higher levels of nitrogen additions can increase their YS to over 400MPa. These steels, called superaustenitic, can contain up to about 0.9 wt% N. To increase the weldability of the nitrogen containing steels, an addition of Mn can be made. Furthermore Mn also partially replaces Ni as an austenite stabilizer and increases nitrogen solubility. Superaustenitic steels can contain up to 8 wt% Mo. This steel offers a very interesting combination of mechanical and corrosion properties: high pitting corrosion resistance combined with an YS of about 450 MPa, tensile strength of about 750 MPa and 40% elongation. Another very efficient alternative to increase the strength of the austenitic stainless steels is work hardening. The low stacking fault energy and the formation of deformation induced martensite give rise to high strain hardening, leading to an YS higher than 1200 MPa, even in the common AISI 304 type. Heating up of work hardened material during weld processing or usage can cause recovery, martensite reversion and even recrystallization, with a consequent loss in mechanical strength. Following Fig.6.6, with the help of a time-temperature-transformation (TTT) diagram, schematically presents the main transformations that occur in austenitic stainless steels during processing or utilization.

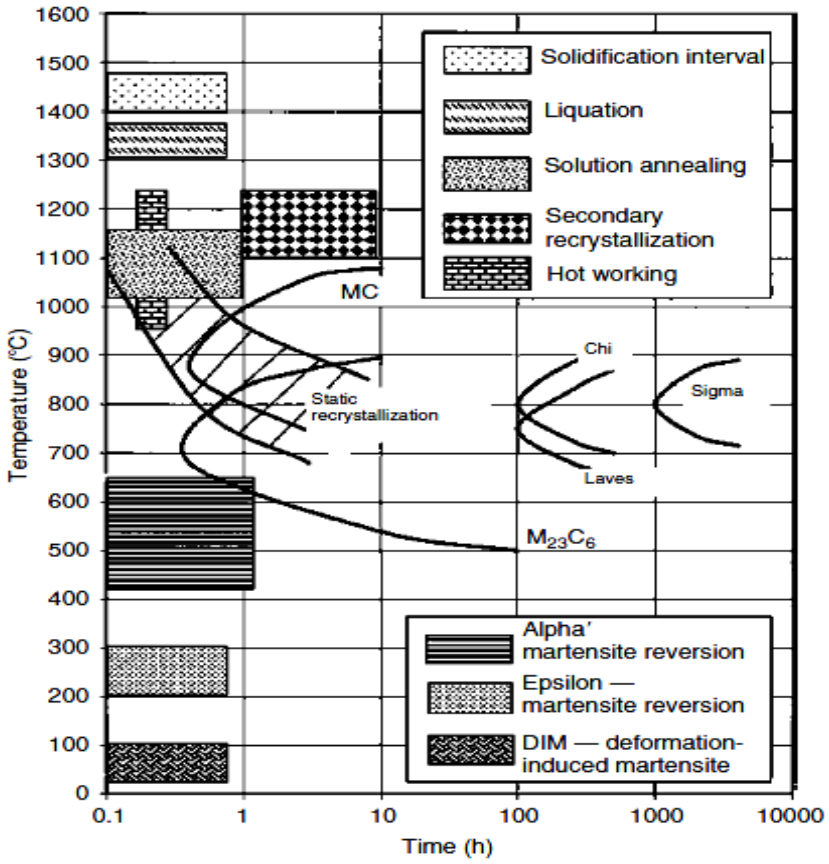



Figure 6.6: Main thermal treatments and transformations that occur in austenitic stainless steels between room temperature and the liquid state.

Before going into the different heat treatments for austenitic stainless steels, it is important to remember two particularly important properties of these steels, namely their low thermal conductivity and high thermal expansion coefficient. The thermal conductivity of the austenitic stainless steels is low; about one fifth of the value for pure iron and one third of the conductivity of an AISI 1025 carbon steel. The thermal expansion coefficient of the stainless steels is about 50% higher than for pure iron or AISI 1025 carbon steel. While the low thermal conductivity limits the heating up and cooling speeds, the high thermal expansion coefficient requires special care concerning the spacing between pieces to be treated.

### 6.4 Solution Annealing

Solution annealing is the heat treatment most frequently specified for austenitic stainless steels, before their actual usage. The main objective of this treatment, as the name implies, is to dissolve the phases that have precipitated during the thermomechanical processing of the material, especially the chromium rich carbides of the $M_{23}C_6$ type (see Fig.6.7), where M/Cr, Fe, Mo.

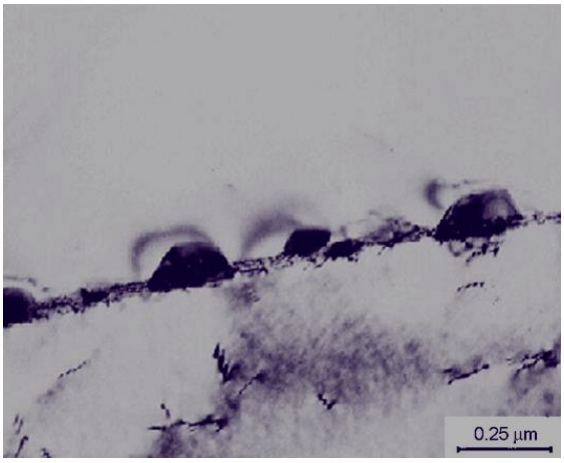



Figure 6.7: Grain boundary $M_{23}C_6$ precipitates in an austenitic stainless steel observed using transmission electron microscopy.

As the precipitation of $M_{23}C_6$ occurs in the 450 to 900$^{o}$C (840 to 1650$^{o}$F) temperature range, the lower temperature limit for solution annealing should be over 900$^{o}$C. Carbides should be completely dissolved but they dissolve slowly. Grain growth limits the maximum solution annealing temperature. In particular, abnormal grain growth, also known as secondary recrystallization, must be avoided. For the more conventional stainless steels, such as AISI 201, 202, 301, 302, 303, 304, 304L, 305 and 308, recommended solution annealing temperatures are around 1010 to 1120$^{o}$C(1850 to 2050$^{o}$F). For higher carbon containing steels such as the AISI 309 and 310 or steels containing molybdenum such as AISI 316, 316L, 317 and 317L, the minimum temperature should be increased to 1040$^{o}$C whereas the maximum should be kept at 1120$^{o}$C (1900 to 20508$^{o}$F). In the case of the stabilized steels (Fig.6), which are more prone to secondary recrystallization or abnormal grain growth, as compared to the nonstabilized steels, the solution annealing temperature range should be at a lower level, between 955 and 1065$^{o}$C

(1750 and 1950$^{o}$F), for titanium stabilized AISI 321 type and narrower, between 980 and 1065$^{o}$C (1800 and 1950$^{o}$F), for the niobium stabilized AISI 347 and 348 (nuclear grade) types. After solution treatment, cooling from heat treatment temperatures should be sufficiently fast to avoid chromium carbide precipitation. On the other hand, too fast cooling rates cause component distortions.

### 6.5 Stabilizing Annealing

Stabilizing annealing is used for stabilize the austenitic stainless steels in order to assure maximum intergranular corrosion resistance. After the solution annealing treatment, only part of the carbon is bound in the form of primary phases, such as carbides, MC, carbonitrides, M(C,N), nitrides MN, or carbosulphides $M_4C_2S_2$, where M/Ti, Nb, or V. The remaining carbon stays in solid solution and may precipitate as secondary carbides MC or $M_{23}C_6$ at lower temperatures, since the carbon solubility in austenite under 900$^{o}$C (1650$^{o}$F) is very low. The precipitation start temperature of the thermodynamically more stable MC carbides is displaced to higher temperatures if compared to the precipitation start temperature of the less stable Cr rich carbides of the $M_{23}C_6$ type. Therefore, exposing the steel, after solution annealing, to temperatures in the 845 to 955$^{o}$ C (1550 to 1750$^{o}$F) temperature range for up to 5h (depending on component size), favours MC precipitation in detriment to $M_{23}C_6$. Furnace atmosphere control, avoiding carburizing or excessively oxidizing conditions, should be employed and the sulphur content in oil or gas fired furnaces should be kept at low levels.

### 6.6 Stress Relief Annealing

The most effective way to relieve stresses is to cool the component slowly from the solution annealing temperature. During slow cooling, some $M_{23}C_6$ precipitation may occur with consequent sensitization. On the other hand, fast cooling may reintroduce residual stresses and make the component susceptible to stress corrosion cracking (SCC). In general, a small amount of intergranular corrosion is causes a failure in few weeks due to SCC. So, stress relief is essential, which is done at a relatively lower temperature range, between 425 and 550$^{o}$C (800 and 1000$^{o}$F), where $M_{23}C_6$ precipitation is very slow, allowing the material to be exposed for some hours without sensitization occurrence. This treatment may not be very efficient to reduce residual stress, nevertheless, it may be sufficient to reduce residual stress sufficiently with subsequent reduction in the risk of SCC.

### 6.7 Bright Annealing

All austenitic stainless steel types can be bright annealed in pure hydrogen or dissociated ammonia atmosphere, below -50$^{o}$C. For doing this the components should be very dry and clean before entering the furnace. If the temperature is not kept sufficiently low, some thin green oxide film may be formed, which will be difficult to remove.

### 6.8 Martensite Formation

Austenite in stainless steels in general and the austenite in the 300 steels series in particular is not a stable phase. In the solution annealed condition, the $M_s$ temperature is normally below the room temperature. For the majority of these steels, the $M_d$ temperature (the temperature below which martensite will form under deformation) is above room temperature. Two kinds of martensite can occur in stainless steels: α' (bcc, ferromagnetic) and ε (hcp, nonferromagnetic). The transformation of austenite to martensite can be also induced in austenitic stainless steels by cathodic charging with hydrogen. During $\gamma \rightarrow \alpha'$ transformation a volume increase of 2.57% and the $\gamma \rightarrow \varepsilon$ transformation causes a volume decrease of 0.81%.

### 6.9 Transformation in Cooling

There are several empirical equations that relate the $M_s$ temperature to the chemical composition. Eichelman and Hull's is one of the most widely used as follows (compositions are in wt%):

$$M_s\ (^oC) = 1302 - 42\ (\%Cr) - 61\ (\%Ni) - 33\ (\%Mn) - 28\ (\%Si) - 1667\ (\%\ [C + N])$$

So, by selecting proper media for subzero treatment media such as liquid nitrogen (-196$^o$C), dry ice (-79$^o$C), liquid helium (-269$^o$C), etc it is possible to transform the austenite phase in ASS to martensitic structures. Above equation suggests that steels, when cooled to cryogenic temperatures, will form alpha prime (α') martensite. The ability to form alpha prime this martensite becomes more significant during cooling after sensitization. $M_{23}C_6$ precipitation at grain boundaries causes depletion of chromium, carbon and other alloying elements in the vicinity of the grain boundaries. This leads to a higher $M_s$ temperature, making the material more susceptible to the formation of alpha prime (α') martensite close to grain boundaries during cooling. For epsilon (ε) martensite no equation like above is reported. However, it is reasonable to expect that the formation of epsilon martensite increases with a decrease in the stacking fault energy of austenite.

### 6.10 Strain Induced Transformation

The most frequent case of martensite formation at room temperature in stainless steels is that of strain induced martensite. The formation and the amount of alpha prime and epsilon depend on steel composition, on its stacking fault energy and on the temperature, amount, and rate of deformation. According to Kaieda and Oguchi, the amount of α' depends also on the stress state during deformation. There are several empirical equations that relate the $M_d$ temperature with the chemical composition. One of the most widely used relation is due to Angel as given below:

$$M_d(30/50)(^oC) = 413 - 13.7\ (\%Cr) - 9.5\ (\%Ni) - 8.1\ (\%Mn) - 18.5\ (\%Mo) - 9.2\ (\%Si) - 462\ (\%\ [C + N])$$

where compositions are in wt%. $M_d(30/50)(^oC)$ is the temperature at which 50 vol% α' is formed after a true tensile strain of 30%. For the majority of austenitic stainless steels, the $M_d$ temperature is above room temperature. For epsilon (ε) martensite such empirical equations are not available. Susceptibility of the austenite to form martensite and the amount of martensite formed increases with decreasing deformation temperature. When stainless steels containing deformation induced martensite are annealed, the martensite may revert to austenite. This reversion usually occurs at temperatures about 100°C lower and for shorter times than those required for the recrystallization of the deformed stainless steel. The formability of the austenitic alloys is influenced greatly by martensitic transformation during straining. When the specimen is stressed beyond the critical stress for martensite formation, the amount of martensite transformed is increased with increases in stress and strain. The kinetics of deformation induced martensitic transformation has usually been treated as a function of strain ε. Ludwigson and Berger proposed that:

$$V_{\alpha'} = A_1 \varepsilon^B V_\gamma$$

$V_{\alpha'}$is volume fraction of martensite, $V_\gamma$ is the volume fraction of austenite, $A_1$ is a constant (less than unity) and B ~ 3 for stainless steels.

**Try to Use Stress Induced Martensite Transformation concept in HT Design of ASS.**

### 6.11 Processing and Heat Treatment of Ferritic Stainless Steel

Ferritic stainless steel ingots have a coarse grain size, are relatively brittle and thus should not be submitted to thermal shocks. Cast plates are ground, slowly heated and hot rolled into strips. The hot rolled coils are then annealed, slit and pickled. Cold rolling, used to obtain intermediate gages, is followed by recrystallization annealing. Ferritic stainless steels are normally used only after solution annealing. The solution annealing temperature varies substantially according to the steel type. The first generation steels are treated at lower temperatures, for example, AISI 430 steel is treated in the 705 to 790°C (1300 to 1450°F) temperature range and the AISI 446 in the 760 to 830°C (1400 to 1525°F) range. The second generation steels are treated at somewhat higher temperatures, for example, AISI 409 is treated in the 870 to 925°C (1600 to 1700°F) range. The third generation steels, such as the AISI 444, are treated at even higher temperatures, in the 955 to 1010°C (1750 to 1850°F) range. Steels with higher chromium contents, such as the superferritic, should be water cooled in order to avoid the 475°C embrittlement due to alpha prime (α') formation. Ferritic stainless steels can be cold worked by most of the mechanical working processes. In comparison with the austenitic stainless steels, the ferritic steels have higher YS before work hardening, lower ductility and, therefore, considered to be less workable than the austenitic steels.

## 6.12 Duplex Stainless Steel

Duplex stainless steels present high levels of alloying elements, such as chromium, nickel, molybdenum and nitrogen, which should be properly balanced in order to achieve similar volumetric fractions of both phases and to give, both ferrite and austenite, a proper corrosion and mechanical resistance. The YS in these steels is more than twice that of the single phase stainless steels either ferritic or austenitic. They also have superior toughness and ductility when compared to the ferritic and martensitic types, in addition to superior intergranular and stress corrosion resistance in comparison to the austenitic type. This favourable combination of properties makes this class of stainless steels widely employed in oil and gas, petrochemical, pulp and paper, and pollution control industries. They are frequently used in aqueous solutions containing chlorides, where they have substituted with advantage (major reductions in weight and welding time) the austenitic stainless steels that are more susceptible to stress and pitting corrosion.

Duplex steels of lower carbon content solidify in a ferritic structure and the austenite forms in the solid state (Fig.6.8 below).

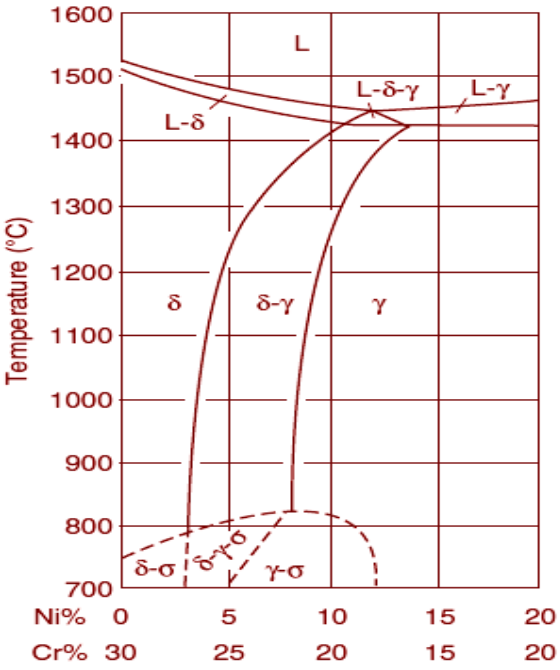



Figure 6.8: Section of the ternary Fe–Cr–Ni (in wt%) diagram at 65 wt% Fe.

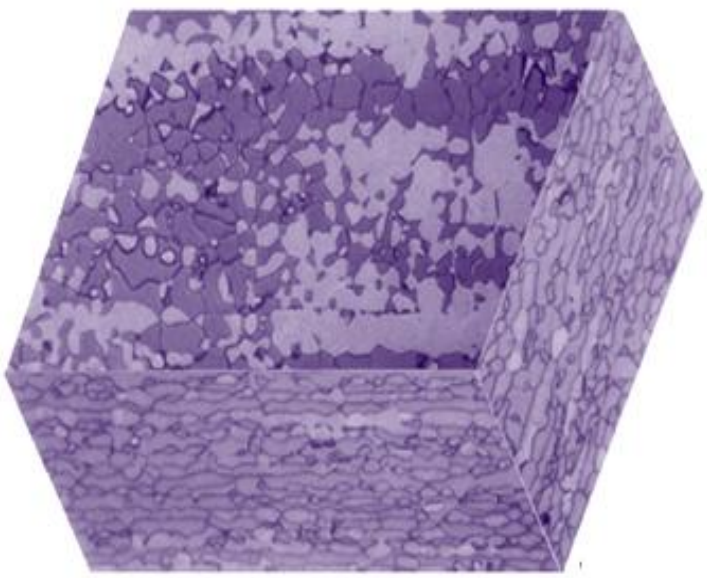


Figure 6.9: Three dimensional composed micrograph of rolled duplex stainless steel.

During hot working, between 900 (1650$^{o}$F) and 1200$^{o}$C (2200$^{o}$F), a microstructure forms with alternating ferrite and austenite lamellae, Fig.6.9.

After solidification, the volume fraction of austenite and ferrite are almost the same. Below 1000$^{o}$C (1830$^{o}$F) the proportion of ferrite to austenite can be only slightly modified. Ferrite

strengthening occurs by solid solution hardening with preferential participation of chromium, molybdenum and silicon, whereas, austenite is stabilized and strengthened by nitrogen. In the case of duplex steels with higher carbon content, the first phase that solidifies is also ferrite. The residual liquid enriched in carbon solidifies forming austenite and a chromium rich $M_{23}C_6$ type carbide network. This carbide network within the austenite leads to an improved wear resistance. During cooling, austenite islands can also form in the ferrite grains.

Some secondary carbide may also precipitate in austenite in the solid state. With the application of mechanical stresses, these carbides initiate fractures and cracks that propagate along the carbide network (see micrograph, Fig.6.10).

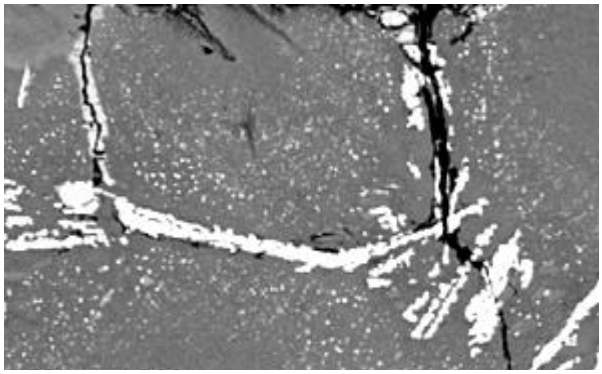


Figure 6.10: Crack propagation along carbide network in the high carbon duplex stainless steel.

The schematic TTT diagram (Fig.6.11 below) shows the regions in which sigma (σ) precipitation can occur. These precipitates increase the hardness and decrease ductility and the toughness. It must be pointed out that σ phase precipitates within the ferrite. In comparison to austenitic and ferritic stainless steels, precipitation of σ phase in duplex alloys occurs at shorter times, at higher and larger volume fractions may be formed.

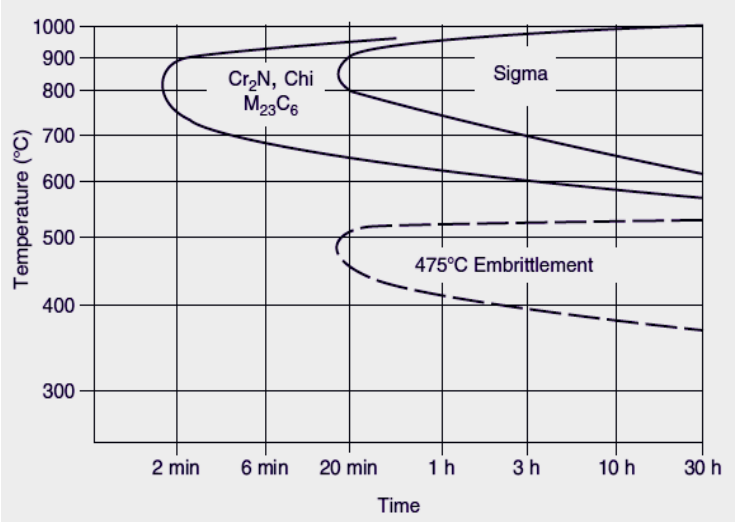



Figure 6.11: TTT diagram showing precipitation of sigma (σ) and other phases in duplex stainless steels.

The favourable combination of properties of duplex steels is intrinsically related to its microstructure. These steels solidify with ferritic structure and the austenite is formed in the solid state. Austenite nucleates at about 1300°C (2370°F) and grows first at the ferrite grain boundaries and later within the ferrite grains. Solidification cracks are rare and castability is excellent. Recrystallization kinetics are faster in ferrite than in austenite, despite the higher driving force for the recrystallization in austenite. During hot deformation, at temperatures between 1000 (1830°F) and 1200°C (2190°F), alternate layers of ferrite and austenite are developed in the microstructure. Phase volumetric fractions must be nearly equal and the volumetric fraction of the minor phase should not be lower than 30%. It must be remembered that the volume fraction of each phase is a function of composition and heat treatment. Furthermore, alloy compositions are adjusted to obtain equal amounts of ferrite and austenite after solution annealing at about 1050°C (1900°F). Cooling from the solution annealing temperature should be sufficiently fast, generally into water, in order to avoid precipitation (see TTT diagram above), especially the 475°C (885°F) embrittlement due to alpha prime (α'). After welding, the solution annealing treatment is recommended, followed by proper cooling.

The precipitations of α' in ferritic and duplex stainless steels are rich in chromium, have a cubic structure, are coherent with ferrite, and have an enormous coalescence resistance, even for very long exposure times at the 350 to 550°C (660 to 1020°F) temperature range. This type of embrittlement leads to a cleavage fracture in the ferritic regions (see micrograph, Fig.6.12). Ductility is determined by the austenitic regions and is portrayed by the dimple like fracture. Austenite volume fraction also plays an important role. Increasing chromium content in the alloy (and thereby the ferrite volume fraction) raises the sensitivity of the material to this type of embrittlement. Although the extent of embrittlement increases with aging time in the 350 to 550°C temperature range, the maximum occurs at about 475°C (885°F).

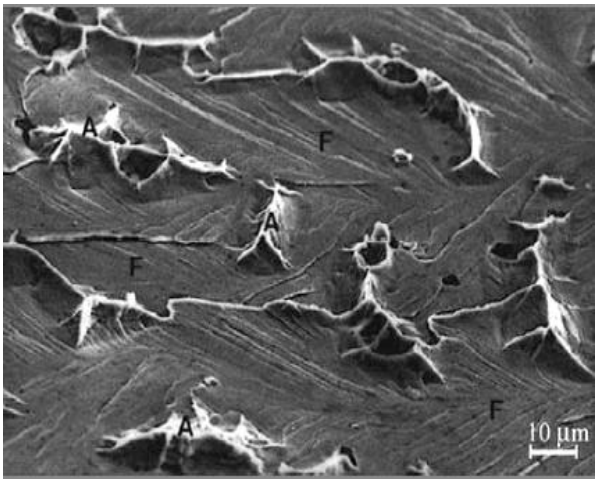



Figure 6.12: Ferrite brittle cleavage fracture (475°C embrittlement) caused by alpha prime (α') in a duplex stainless steel. Scanning electron microscopy with secondary electrons. A=austenite; F=ferrite.

## 6.13 Martensitic Stainless Steels

Martensitic stainless steels are essentially Fe-Cr-C alloys, containing chromium in the range of 11.5 to18wt% and carbon in range of the 0.1 to1.2wt%. As chromium level is increased, carbon level has to increase also in order to stabilize austenite (see Fig.6.13).

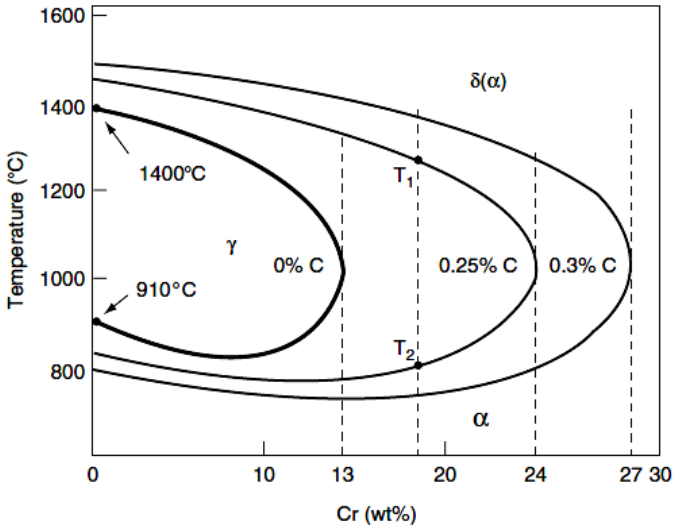



Figure 6.13: Effect of carbon and chromium on the gamma phase portion of Fe-C-Cr ternary diagram.

For the martensitic steels, it is, of course, essential to form austenite from which martensite is obtained on cooling. For example, for a complete austenitization, steels containing 13wt% chromium needs to have carbon content in excess of 0.15wt% carbon and to be heated to at least 950°C. Steels containing more chromium, say17wt%, need to have carbon content higher than 0.3wt% carbon and to be heated to at least 1100°. As mentioned previously, both nitrogen and nickel expand the γ-loop, Fig.6.14.

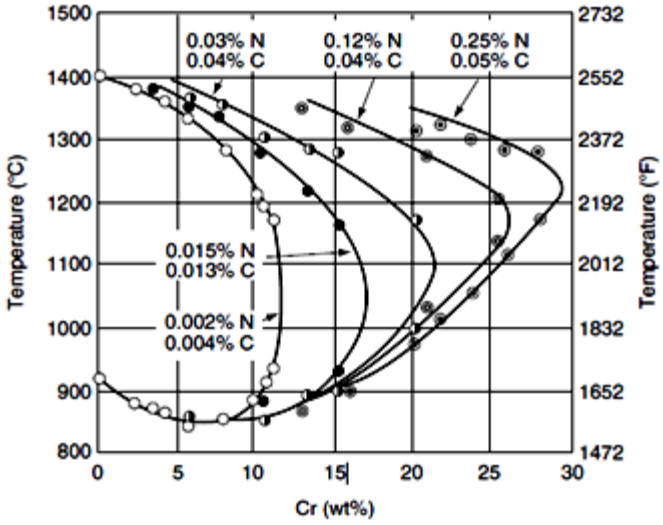



Figure 6.14: Effect of nitrogen on the gamma loop.

Other alloying elements frequently observed in martensitic stainless steels are nickel and molybdenum. Nickel entitles the usage of lower carbon contents and, as a consequence, higher toughness and corrosion resistance may be obtained. For soft but tougher martensitic steels containing lower carbon levels, nickel content may reach 5wt%. These soft martensitic steels are frequently precipitation hardened as will be discussed in the next item. Molybdenum also improves corrosion resistance, in addition to improvement in toughness. It must be remembered that corrosion resistance in martensitic stainless steels is significantly lower if compared to other stainless steels discussed previously in this chapter. They are inadequate for usage in more aggressive media. The most popular composition (AISI 410) contains about 12.5 wt% chromium and 0.1wt% carbon. In the hardened condition, its YS may reach about 1300MPa, however upon tempering at higher temperatures its strength decreases significantly. The YS attained by a martensitic stainless steel depends mainly on its carbon level and some compositions may reach YS of the order of 1900MPa. The maximum chromium level is about 18wt% and some compositions have up to 1wt% molybdenum. As mentioned previously, both Cr and Mo shrink the austenitic field, which may be expanded by C and Ni. For example, a steel containing 17wt% chromium and 0.2 wt% carbon will require 2wt% nickel to avoid delta ferrite formation.

Prior to final hardening and tempering heat treatments, martensitic stainless steels are annealed in order to be machined and cold worked. For example, an AISI 410 is annealed in the 750 to 900$^{o}$C temperature range for 2 to 4h and furnace or air cooled. In such a condition, hardness is about 160 HB, YS of 300 MPa, tensile strength of 500 MPa, elongation of 20%, with an area reduction of 60%. Prior to their final usage, martensitic stainless steels are submitted to the same heat treatment sequence as that for carbon steels, namely they are austenitized, hardened by quenching, and tempered in order to improve ductility and toughness. At high temperatures, their stable structure is austenitic and at room temperature it is a stable mixture of ferrite and carbide. As the stainless steels have a low thermal conductivity, depending on the cross-sectional size and complexity, preheating in the 550 to 800$^{o}$C temperature range, prior to final austenitizing temperature, is recommended. Air heating may cause decarburization.

The formation of a more stable (ferrite + carbides) microstructure is very sluggish (see Fig.6.15) and the tendency toward martensite formation (high hardenability) is very high. Therefore, the majority of martensitic stainless steels form martensite on air cooling, even for sections that are up to about 300mm in thickness. Hardening media may be air or oil. While oil cooling is preferred in order to avoid carbide precipitation, air cooling may be needed to avoid distortions in more complex sections. Martempering is also possible in this class of steels. Martensite hardness depends essentially on carbon content varying from about 35HRC for a 0.1 wt% C to 60 HRC for 0.5wt% C, there on increasing little for C higher than 0.5wt%. For low carbon martensitic steels, such as the AISI 410, the $M_s$ and $M_f$ temperatures are relatively high, 350 and 250$^{o}$C, respectively and decrease with increasing carbon content. High carbon steels may present

retained austenite and a subzero treatment around -75°C, immediately after hardening, is recommended.

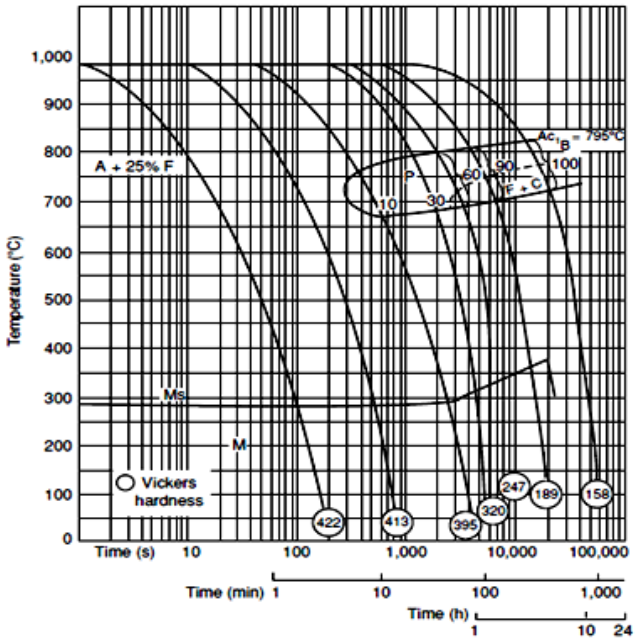



Figure 6.15: Continuous cooling transformation diagram.

Double tempering is also very common. Tempering temperature is determined by the required mechanical properties. In general, the 420 to 600°C temperature range must be avoided, because within this range brittleness may be induced apart from loss in corrosion resistance, Fig.6.16.

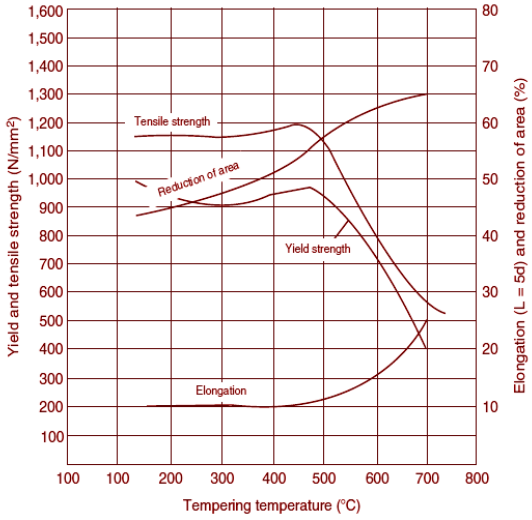



Figure 6.16: Effect of tempering temperature effect on mechanical properties

### 6.14 Precipitation Hardenable (PH) Stainless Steels (SS)

This steel was developed to offer high mechanical resistance and reasonable toughness, with superior corrosion resistance when compared to the martensitic steels of the Fe-Cr-C system. PH stainless steels may be classified according their microstructure resulting from the solution

annealing heat treatment into austenitic, semiaustenitic and martensitic SS. Semiaustenitic steels will transform into martensite during subsequent heat treatments. Practically all PH steels have a low carbon level (≤0.1wt%) with nickel additions. Mo is added to increase mechanical and corrosion resistance. PH is attained through additions of Al, Ti, Ni or Cu.

In a majority of the cases they are intermetallic phases that are rich in nickel, of the $Ni_3M$ type, where M=Al, Ti, Nb, or Mo. Titanium and niobium are also nitride and carbonitride formers which are very stable and are of the MN and M(C,N) types, taking carbon and nitrogen out of solid solution. Copper, in addition to causing hardening through precipitation, enhances corrosion resistance when in solid solution. Aging in the temperature range 450 to 575$^{o}$C leads to finely distributed coherent particles of NiAl. The mean size of the particles, even after aging at 625$^{o}$C for 4h, was about 70A°. Thus, these precipitates were found to be highly resistant to overaging. Compared to martensitic stainless steels of the Fe-Cr-C system, PH steels present a superior ductility and toughness. Some alloys have YS of up to 1700 MPa. Relative to other stainless steel types, PH steels have a moderate to good corrosion resistance.

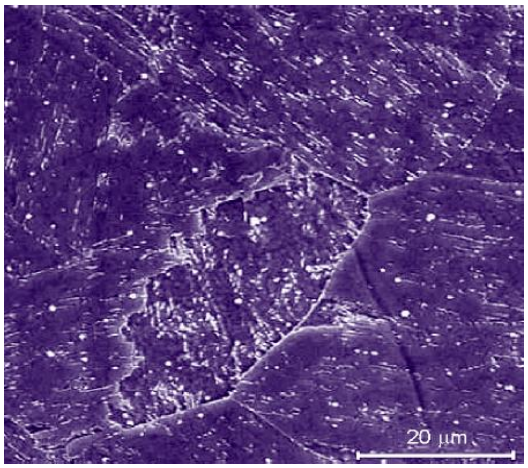



Figure 6.17: Scanning electron microscopy using secondary electrons to illustrate carbide precipitation.

PH steels that form martensite can be subdivided into two groups, namely single heat treatment (martensitic) stainless and double heat treatment (semiaustenitic) stainless steel. The alloys that require a single heat treatment are solution annealed at about 1040$^{o}$C, leading to a martensitic microstructure without retained austenite at room temperature. Then these alloys are precipitation aged by intermetallic phases, through tempering in the 480 to 620$^{o}$C temperature range. The properties obtained depend mainly on the alloy chemical composition and tempering treatment procedure. For example, for a 17-4 PH alloy, after aging for 1h at 480$^{o}$C, YS may reach 1310 MPa and after 4h aging at 620$^{o}$C, YS is only 930MPa. Typical examples of these alloys are the 17-4 PH, 15-5 PH, and custom 450 types. Micrographs shown in Fig.6.17 illustrate the typical microstructure of a martensitic stainless steel of this type (15-5PH) after quenching and tempering.

Alloys requiring double heat treatment are semiaustenitic, which after solution annealing, remain austenitic. A typical example of this group is the 17-7 PH, which is hardened in water from 1065$^{o}$C. Austenite conditioning is performed at about 760$^{o}$C in order to precipitate (mainly the $M_{23}C_6$ carbides) destabilizing austenite so that it transforms into martensite on cooling under 15$^{o}$C. Then aging is performed in the 565 to 595$^{o}$C temperature range, leading to a tensile strength from 1030 to 1240MPa. Another alternative aiming at austenite conditioning is to perform the heat treatment conditioning at a higher temperature, typically 955$^{o}$C, where less carbides precipitate, austenite destabilization is less accentuated and martensite transformation requires a subzero (-75$^{o}$C) treatment.

# Chapter Seven

## Heat Treatment of Nonferrous Alloys

### 7.1 Introduction

There are several methods that may be used to increase the strength of a metal; alloying, quenching, work hardening and one very specific form of heat treatment, that of precipitation or age hardening (the two terms are synonymous). Many ferrous and nonferrous alloys are capable of being age hardened and as the name suggests, this method of increasing the strength relies upon the formation of precipitates. To achieve the optimum combination of mechanical properties the heat treatment cycles must be very closely controlled. In this chapter, precipitation hardening of some important nonferrous alloys will be discussed.

The precipitation hardening mechanism requires the solubility of the alloying element, the solute, in the solvent, to increase as the temperature increases as shown in the phase diagram in Fig.1, where the solvus line shows decreasing solubility of alloying element. At first the cast or wrought alloys is heated to a temperature where a single solid solution is achieved. The holding time needs to be sufficient to make a fully homogeneous solid solution. After this, the solid solution is quenched in a suitable media as shown in the Fig.7.1. Then the solid solution is aged a suitable temperature to form fine intermetallic compounds that make the alloy hardened.

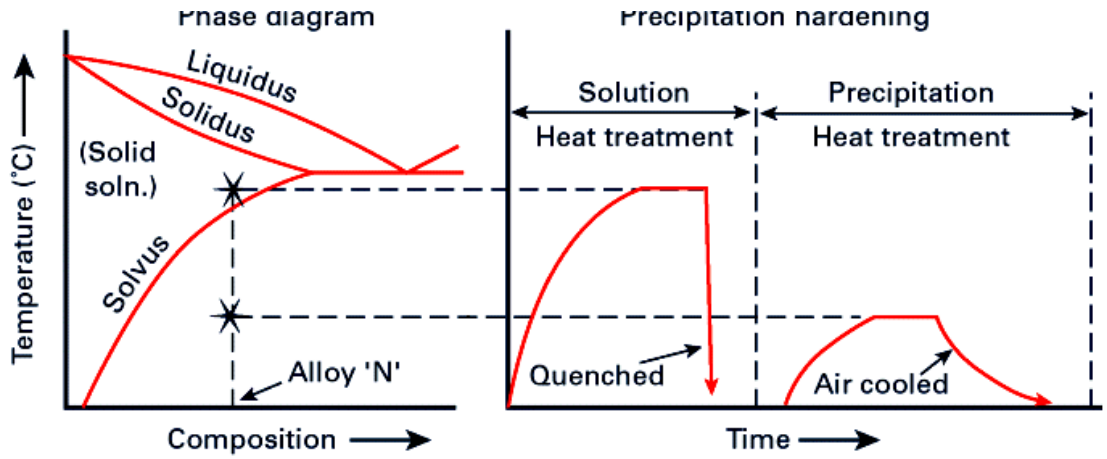



Figure 1: Typical heat treatment schedule for nonferrous alloy.

While this alloy is allowed to stay at room temperature for five to seven days, the strength enhances significantly due to slow precipitation of submicroscopic particles. These particles are around the grains, mostly uniformly distributed. The time of this precipitation may be decreases to a few hours with heating the quenched alloy to 120$^{o}$C. This is called as artificial age hardening. Close control in both aging time and temperature are important in precipitation

hardening for this reasons. Salt baths at constant temperatures utilize 4%Cu aluminium alloy is most suitable for such type of treatment.

### 7.2 Al-4Cu Alloys

Al-4%Cu alloys in the cast form is very poor in mechanical property because of its inhomogeneous chemical compositions and coarse grains (Fig.7.2). Age hardening significantly improves their mechanical properties. So, it is a very popular heat treatment for Al-4%Cu alloys.

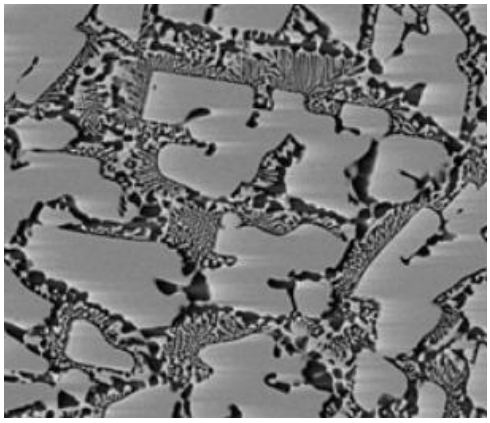


Figure 7.2: Inhomogeneous as cast microstructures of Al-4%Cu alloy.

Now, the process of age hardening will be illustrated with particular reference to aluminium alloys containing 4% copper. Following Fig.7.3 depicts the equilibrium demonstration of Al-Cu system. This is seen that the solubility of Cu in α phase solid solution reduces steadily and slightly considerably along with decrease in temperature. For a certain composition, copper aluminide or $CuAl_2$ such is deposited like coarse particles in and around the grains of α-solid solution. $CuAl_2$ is extremely hard and brittle.

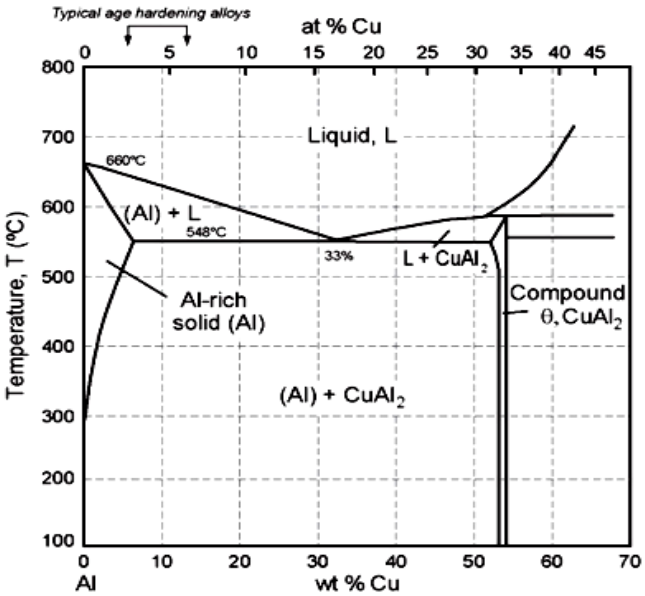



Figure 3: Al-Cu binary phase diagram.

For precipitation hardening (PH), at first, this alloy is reheated to about 550°C, where a uniform chemical composition along with single Al rich α solid solution is formed (point 1 in Fig.7.4 below). This single phase solid solution is then quenched in water to get super saturated solid α, because there is inadequate time for $CuAl_2$ to form and copper atoms are here held in a supersaturated solid solution inside the aluminium (case 2).

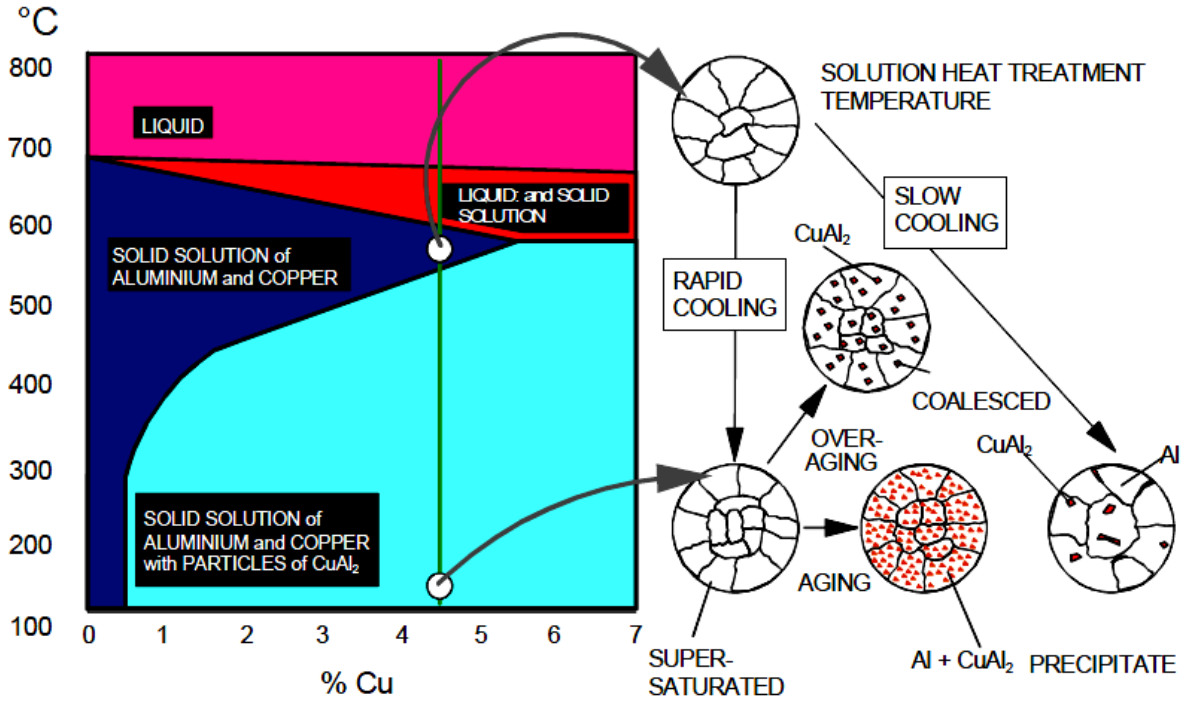



Figure 7.4: Microstructural changes during PH of Al-4Cu alloy

The effects of aging time and temperature on the tensile strength of the Al-4%Cu alloy are shown in Fig.7.5 below.

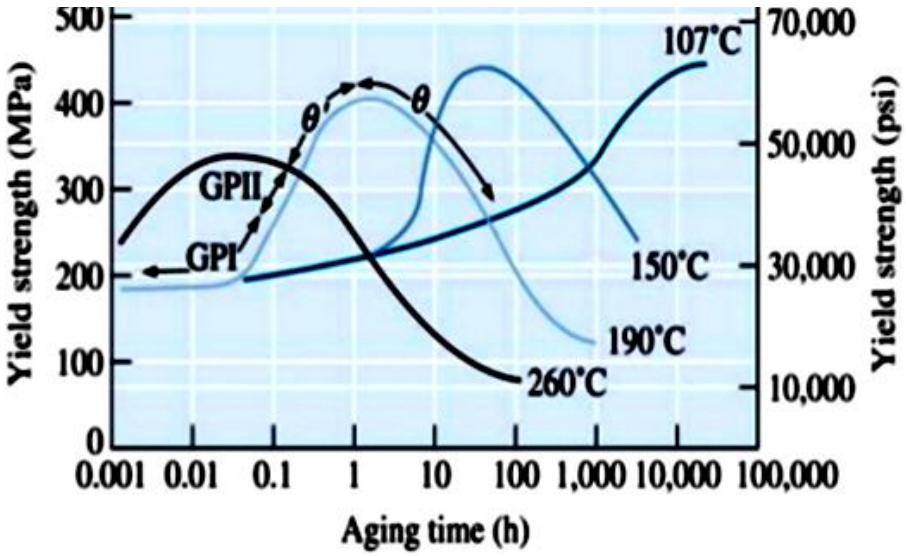



Figure 7.5: Effects of aging time on yield strength of Al-4Cu alloy.

As per the diagram both aging time and temperature have a great effect on the tensile strength of the alloy. Here GP means Guinier-Preston. At relatively low temperatures and in a short time scale where the solute atoms begin to cluster together to form extremely small and very finely dispersed precipitates known as Guinier-Preston (GP) zones, named after the two metallurgists who first identified them. The GP zones are so small that they are not visible using normal optical microscopes but can be seen using electron microscopy at magnifications of around x100,000. After proper PH, the microstructures of Al-4%Cu alloy will have very fine precipitates of $Al_2Cu$ intermetallic compound in the aluminium rich solid solution as shown in the following Fig.7.6.

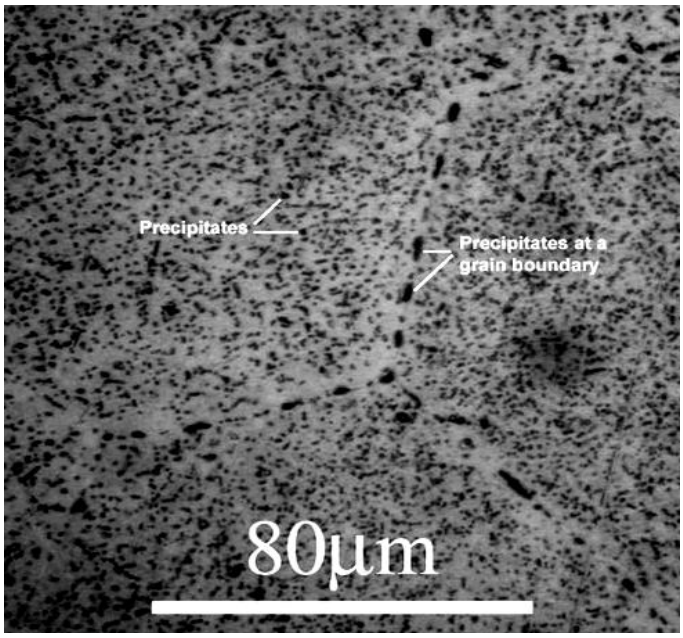



Figure 7.6: Microstructures of PH Al-4Cu alloy.

**Problem 1**: An Al-4%Cu alloy is to be age hardened to get the maximum strength. If the alloy is over aged for one hour, what will be the final strength after completion of age hardening? Consider two different aging temperatures as 190$^{o}$C and 260$^{o}$C.

**Solution**: At 190$^{o}$C, the peak strength of 400MPa (60,000psi) occurs after two hours of aging. After three hours, the strength is essentially the same.

At 260$^{o}$C, the peak strength 340MPa (50,000psi) occurs just after 0.06 hour. However, after 1 hour, the strength decreases to 250MPa (40,000psi).

**Comment**: Higher aging time results lower peak strength and is very sensitive to ppt coarsening and degradation in mechanical properties.

### 7.3 Al-Si-Mg Alloy

By weight, 90% of all shaped Al castings are made from Al-Si based alloys. The phase diagram of the Al-Si system, shown in Fig.7.7, features a eutectic with Si and Al but only very low solubility of Al and Si. Al-Si alloys are used because they combine good casting properties with acceptable mechanical properties, specifically:

a) Si improves the fluidity of Al,
b) Si particles are hard and improve the wear resistance of Al, and
c) by adding Mg, Al-Si alloys become age hardenable through the precipitation of $Mg_2Si$ particles.

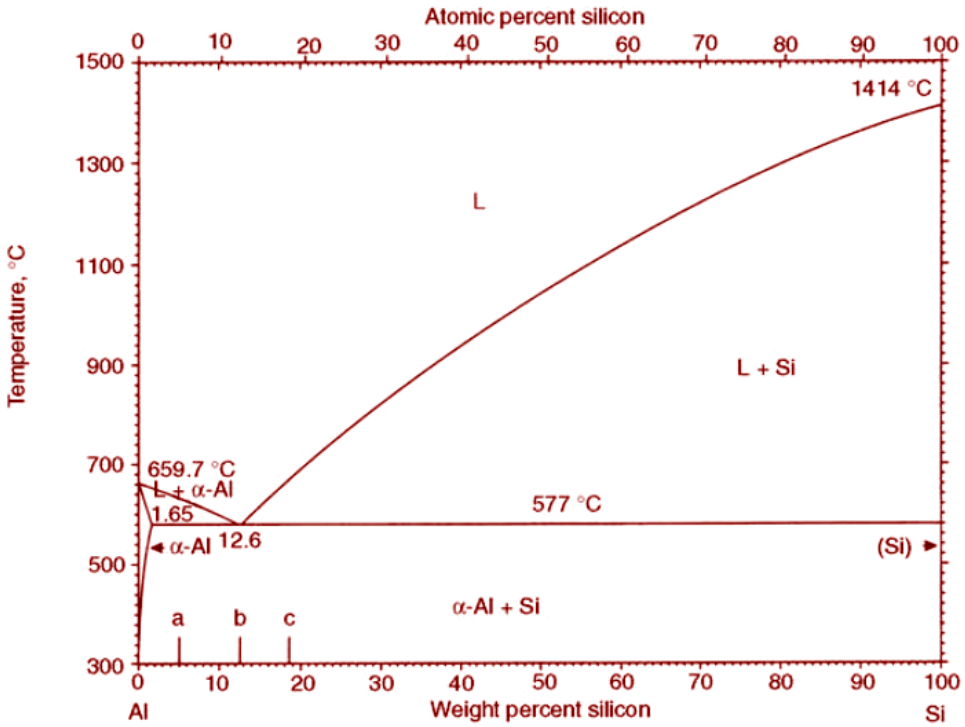



Figure 7.7: Al-Si binary phase diagram.

The microstructures of hypoeutectic (5%Si, left), eutectic (12.6%Si, middle) and hypereutectic cast Al-Si alloys are given below in Fig.7.8.

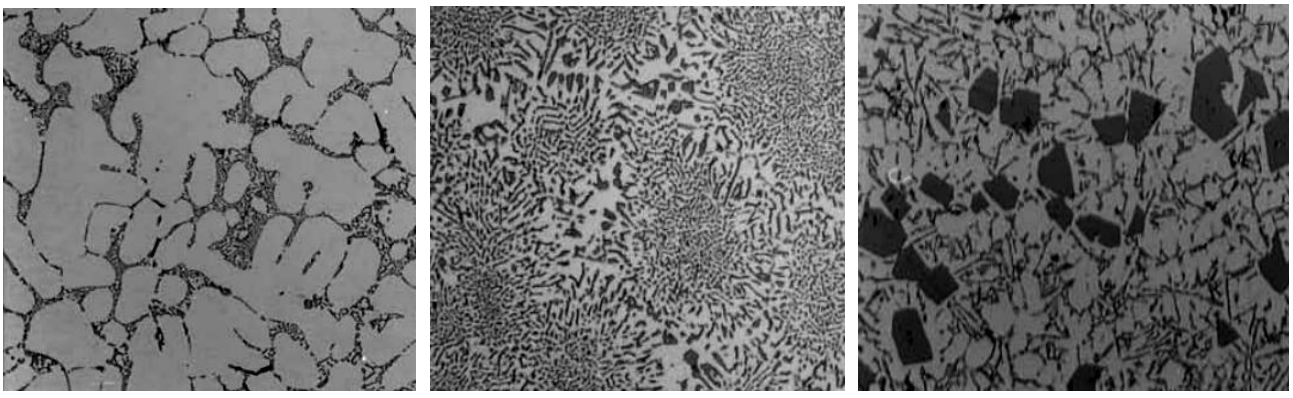


Figure 7.8: Microstructures of Al-Si alloys.

An additional advantage of Al-Si alloys for casting applications is that Si expands on solidification. While the volume of most metals (including Al) shrinks substantially on solidification. Two phase Al-Si alloys contract less, which makes these alloys less prone to pore formation during casting, Table 7.1.

Table 7.1: Volumetric contration of Al and its alloys

| Alloy | Volumetric Contraction on Solidification |
|---|---|
| Al | 6.6 % |
| Al–4.5 %Cu | 6.3 % |
| Al–12 %Si | 3.8 % |

Addition of Mg in Al-Si alloy makes it age hardenable because the solubility of Mg in Al is much higher (Fig.7.9) and during age hardening it form intermetallic compound with Si.

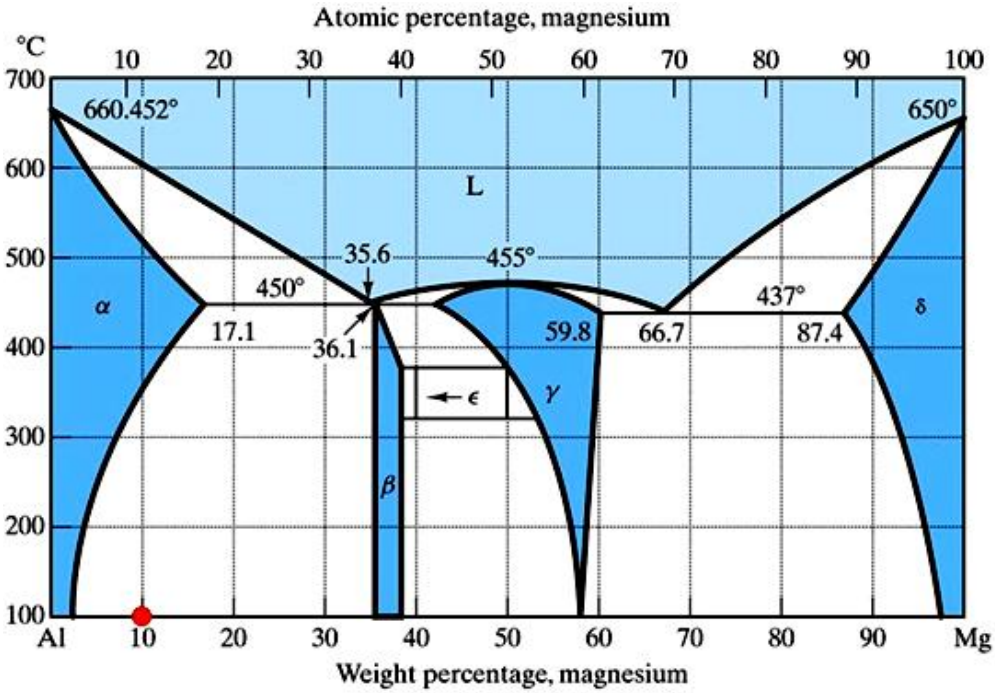



Figure 7.9: Al-Mg binary phase diagram.

### 7.4. Age Hardening of Al-Si-Mg Alloys

In the present experiment, we study the age hardening of Al-7%Si–0.3%Mg alloys. Fig.7.10 given below depicts the equilibrium solubility versus temperature for $Mg_2Si$ in Al with a Mg:Si mass ratio of 1.73:1, while Fig.7.11 displays the solubility versus temperature for Mg and Si in solid Al in equilibrium with $Mg_2Si$ and Si.

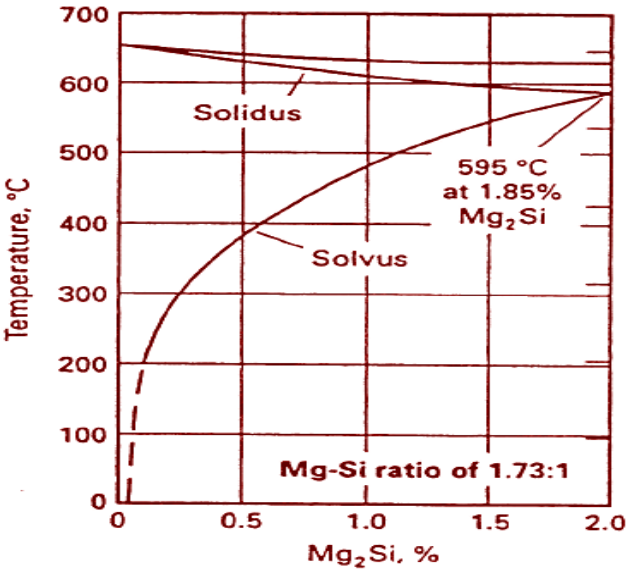



Figure 7.10: Equilibrium solubility versus temperature for $Mg_2Si$ in Al.

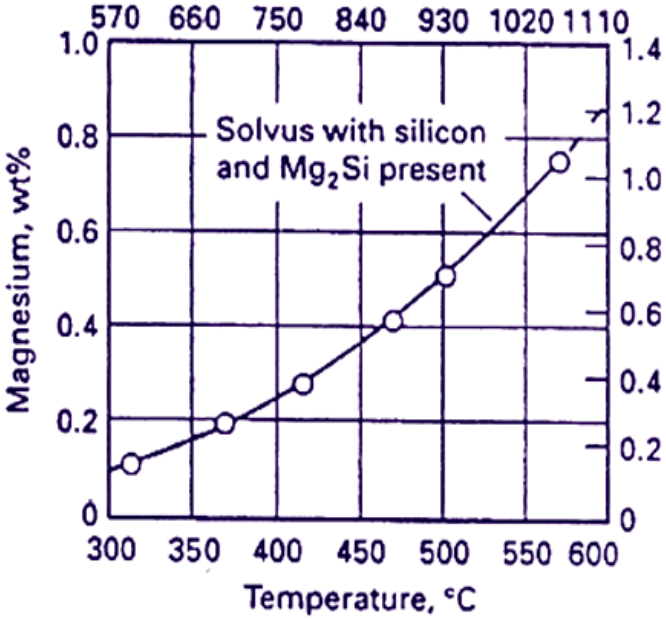



Figure 7.11: Solubility versus temperature for Mg and Si in solid Al equilibrium with $Mg_2Si$ and Si.

After the common thermal treatments, these alloys contain three phases: (i) the Al matrix, (ii) Si (large particles, coarse dispersion) and $Mg_2Si$ (small particles, fine dispersion). The precipitation sequence of alloys with an atomic ratio Mg:Si of 2:1 (mass ratio of 1.73:1) is :

$$\text{supersaturated } \alpha \longrightarrow \text{G.–P. zones} \longrightarrow \beta' \longrightarrow \beta(Mg_2Si)$$

"G–P zones" is an abbreviation for Guinier–Preston zones; an early stage of precipitates characterized by an enrichment of solute atoms (Si, Mg) on the lattice sites of the matrix (Al). In the case of Al-7%Si-0.3%Mg alloys, these first particles have the shape of needles, with a diameter of about 0.1nm and the length of about 10nm. The particles that form in the next stage of the decomposition process, β' particles, already have the composition $Mg_2Al$. The crystal structure is face centered cubic with a lattice parameter of 0.64nm. The particles are rod shaped. They nucleate heterogeneously, preferentially at dislocations in the Al matrix.

The equilibrium phase, β ($Mg_2Si$), finally, has a face centered cubic crystal structure with a lattice parameter of the 0.639nm. It is generally believed that the transformation of β' → β is diffusionless with only minor atomic rearrangements and some change in the degree of coherency between the precipitate and the matrix. If the alloy contains excess Si, large Si particles form in addition to the $Mg_2Si$ particles from the precipitation sequence. Typical microstructures after PH of Al-Si-Mg alloy is shown in Fig.7.12.

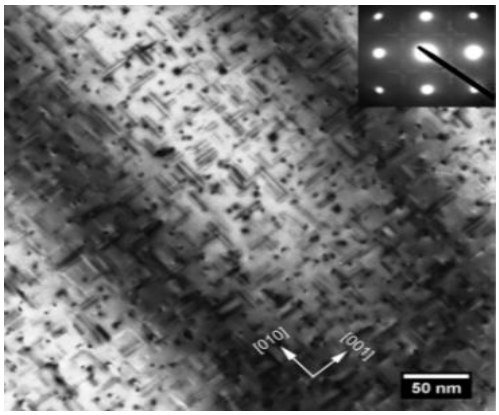


Figure 7.12: Microstructures ofAl-Si-Mg alloy after precipitation hardening.

In order to know the effects of other elements, especially Cu on the PH effect of Al-Si-Mg alloys various amount of Cu was added as shown in Table 7.2 below.

Table 7.2: Various combinations of Al-Si-Mg alloys

| Alloy | Si | Mg | Cu | Ni | Ti | Al |
|---|---|---|---|---|---|---|
| Alloy-1 | 5.902 | 0.461 | 0.007 | 0.005 | 0.099 | Bal |
| Alloy-2 | 6.033 | 0.517 | 0.558 | 0.006 | 0.094 | Bal |
| Alloy-3 | 6.105 | 0.555 | 1.185 | 0.029 | 0.088 | Bal |
| Alloy-4 | 5.801 | 0.497 | 1.980 | 0.003 | 0.094 | Bal |
| Alloy-5 | 5.884 | 0.532 | 3.800 | 0.014 | 0.086 | Bal |

The variation of ultimate tensile strength of alloys 1-5 under various aging conditions are shown in the following Fig.7.13. The test values obtained at a strain rate of $10^{-3}$ $s^{-1}$ were used to plot the graphs. It can be seen that a maximum ultimate tensile strength of 249 MPa was obtained after ageing for 1 hour at 225°C for alloy 4 (2 wt.% Cu). A fall in tensile strength was observed in alloy 5 containing a higher amount of Cu (4 wt% Cu). The UTS decreased gradually in samples aged at temperatures above 225°C. The base alloy (alloy 1) showed lower variation in tensile strength at all aging temperatures.

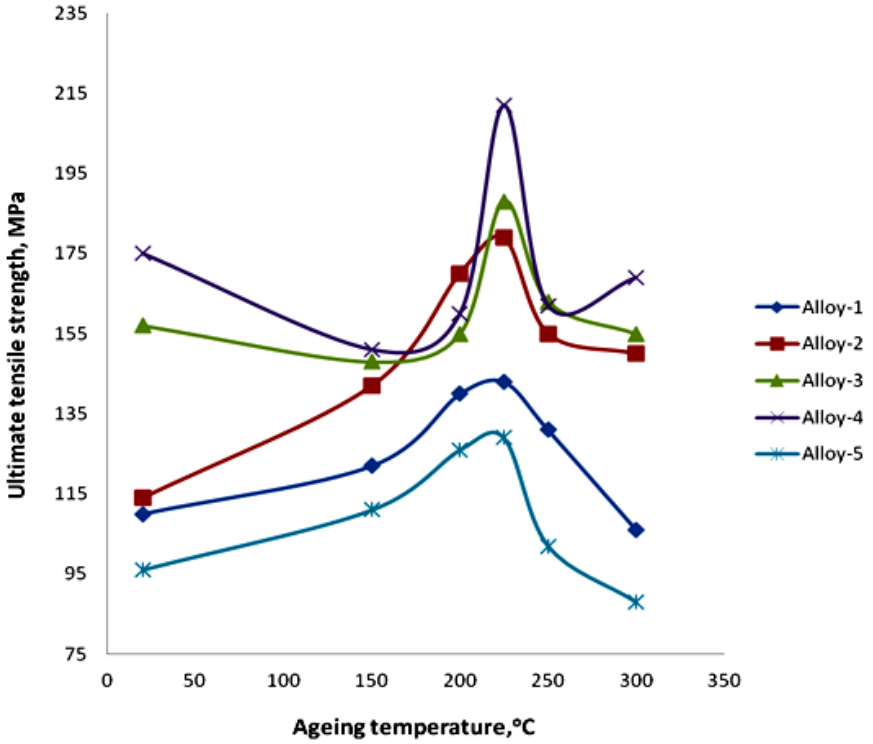
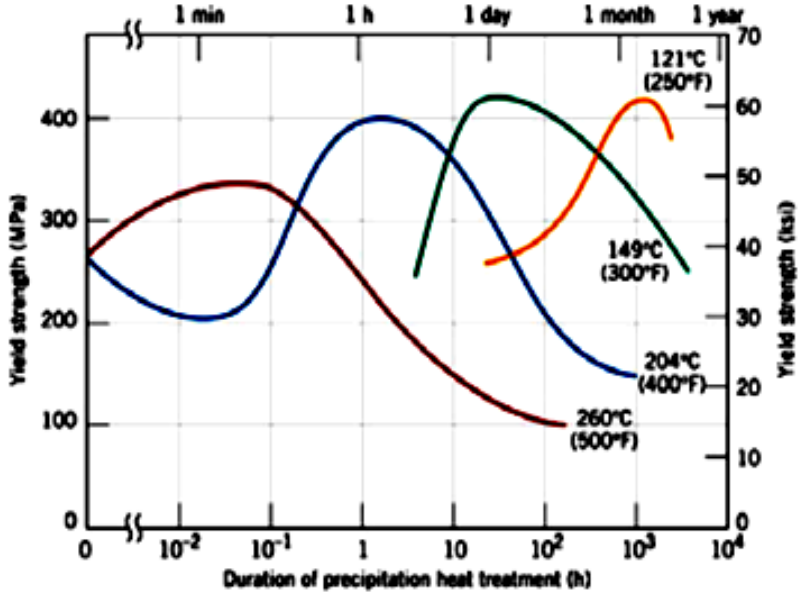



Figure 7.13: Effects of copper on the aging behaviours of Al-Si-Mg PH alloys.

**7.5 Design of PH Treatment for Al-Si-Mg Alooy**: The aging treatment of an Al-0.8Si-0.5Mg alloys are shown in the following Fig. Suggest an economically suitable aging treatment schedule for getting at least 400MPa YS along with better age hardening flexibility.




**Solution:** In the above figure, there are four age hardening temperatures among which aging at 260$^{o}$C is not capable to induce 400MPa YS after any aging time.

Aging at 204$^{o}$C, 149$^{o}$C and 121$^{o}$C are capable to induce the targeted YS level. However, we are asked to select aging temperature that is capable to result minimum 400MPa YS with the maximum level of aging flexibility. In this respect, we should not select 204$^{o}$C aging option because, in this case, before peak value 400 MPa YS will not be achieved, i.e. only peak strength is the targeted strength. Holding at peak strength temperature is not always an easy task. On the other hand, aging at 121$^{o}$C will not be a wise decision as it takes too much time.

So, for the best aging option in the aforementioned Al-Si-Mg alloy for achieving 400MPa YS will be aging at 149$^{o}$C. Here, before peak value, the targeted strength will be achieved and there will be no problem if one crosses the peak temperature or stay below of that value, where still the targeted value will be achieved. Moreover, if excess aging is done by any reason that will still serve the purpose because of very slow strength decrease.

### 7.6 Copper Base Alloy

There are various age hardenable copper base alloys as Cu-Be, Cu-Nb, Cu-Ti, etc. Among these, Cu-Be alloy gives the maximum strength after age hardening. The binary phase diagram of Cu-Be alloy is given below in Fig.7.14.

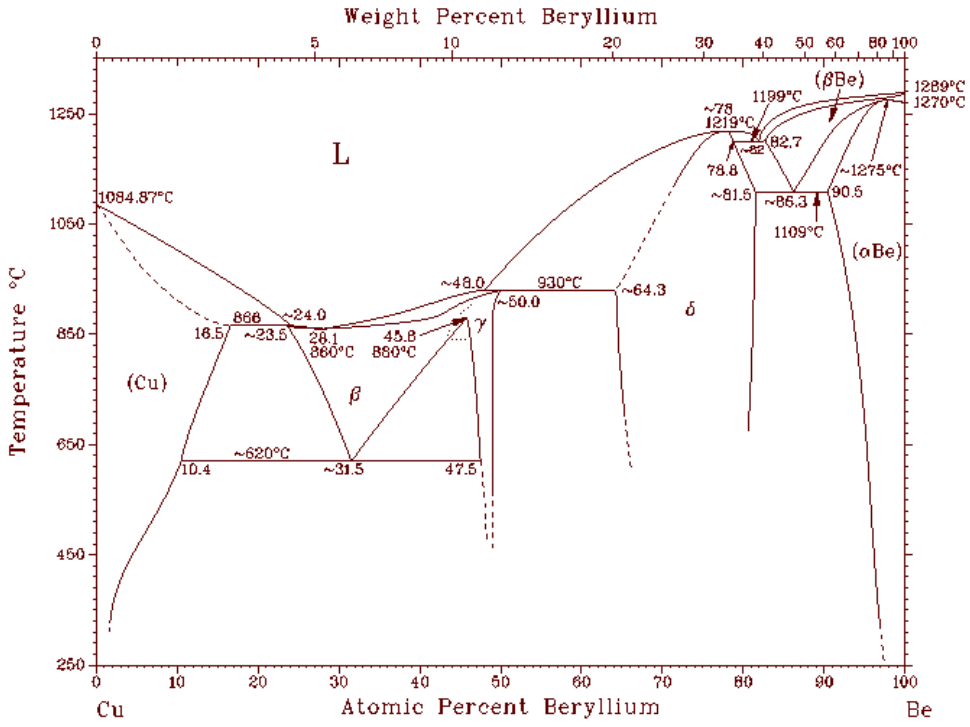



Figure 7.14: Cu-Be binary phase diagram.

Alloy 25 beryllium copper (1.8-2.10% Be, Fig.7.15 below) is an age hardening alloy which attains the highest strength of any copper base alloy. It may be age hardened after forming into springs, intricate forms or complex shapes. It has superb spring properties, corrosion resistance and stability as well as good conductivity and low creep.

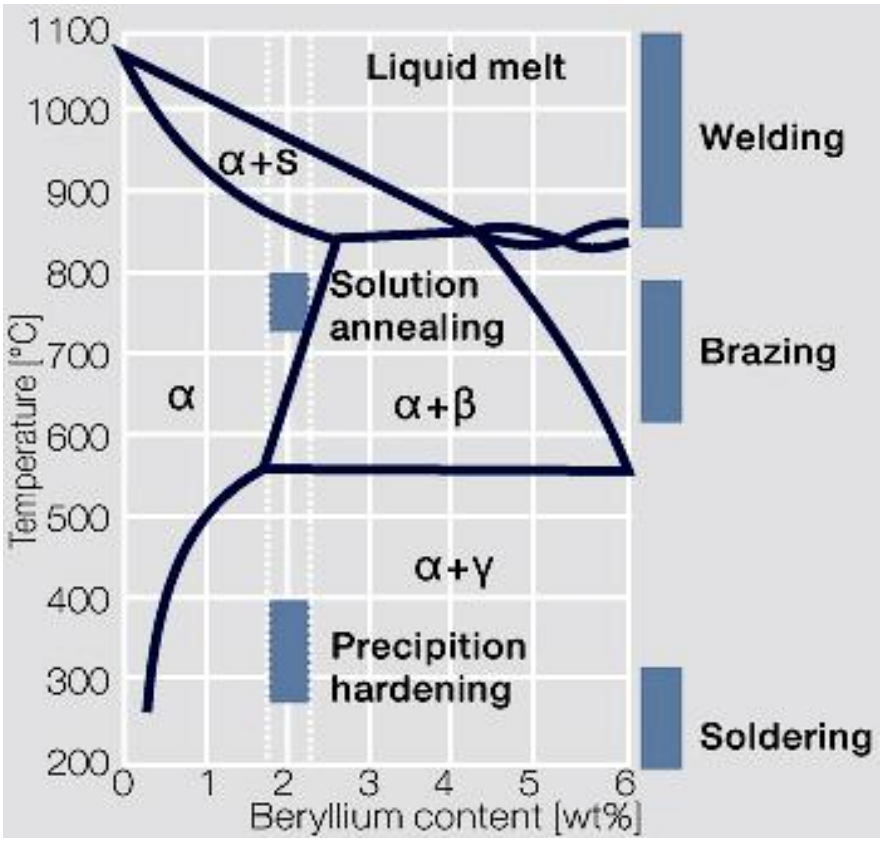



Figure 7.15: PH hardening of Cu-Be alloy.

### 7.6.1 Age Hardening of Copper Base Alloys

Copper beryllium achieves its maximum levels of strength, hardness and conductivity through age hardening. During the age hardening process, microscopic, beryllium rich particles are formed in the metal matrix. This is a diffusion controlled reaction and the strength will vary with aging time and temperature. Recommended or standard age hardening time and temperature combinations have been determined for each copper beryllium alloy. For standard aging temperature (315$^{o}$C or 600$^{o}$F) allow parts to reach peak strength in two to three hours, without the risk of strength decrease due to extended temperature exposure, Figs.7.16 below.

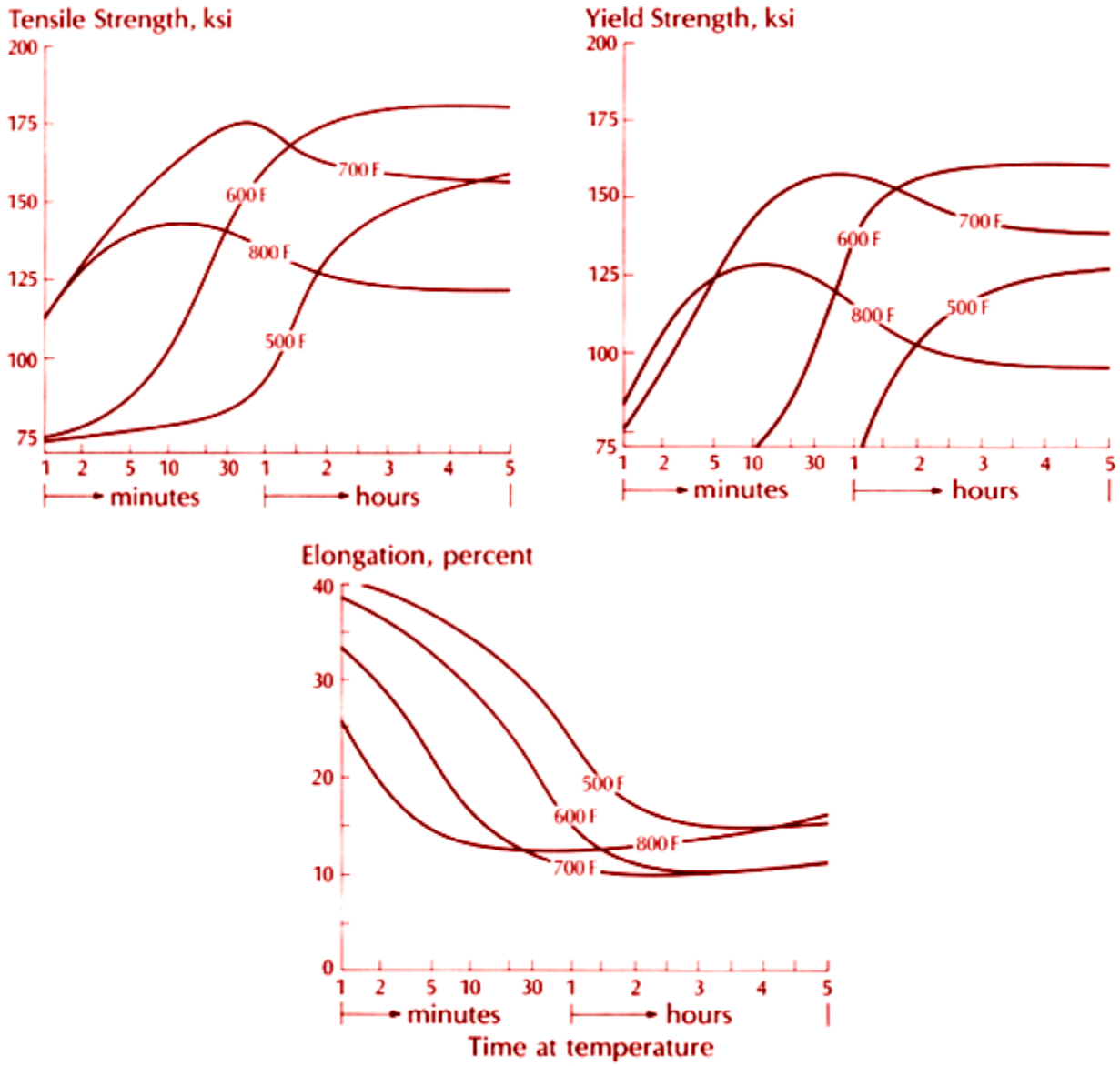



Figure 7.16: Effect of aging temperature on the tensile properties of Cu-Be alloy.

It is to be noted that low, standard and high aging temperatures affect both peak properties and the time required for the alloy to reach peak strength. In the above Fig.7.16, at the low temperature of 550°F (290°C), the strength of the alloy increases slowly and peak strength is not reached until approximately 30hrs. At the standard temperature of 600°F (315°C), the alloy exhibits virtually no change in the strength after three hours of exposure. At 700°F (370°C), peak strength is reached in 30 minutes and declines almost immediately. In short, as aging temperature increases, the time necessary to reach peak strength decreases, as does maximum obtainable strength. This response is similar for all copper beryllium alloys, but at different standard temperatures. Copper beryllium alloy can be age hardened to varying degrees of strength. The term peak aged refers to copper beryllium aged to maximum strength. Alloys not aged to

maximum strength are underaged and alloys aged beyond maximum strength are overaged. Underaging copper beryllium increases toughness, uniform elongation and fatigue strength. Overaging increases the alloy's electrical and thermal conductivity and dimensional stability. Copper beryllium alloy never ages at room temperature, even if material is stored for significant lengths of time.

Allowable variances in age hardening time are dependent on furnace temperature and final property requirements. To peak age at the standard temperature, furnace time is typically controlled to ±30 minutes. For high temperature aging, however, more precise time control is required to avoid overaging. For example, the aging time of Alloy 25 at 700°F (370°C) must be controlled to ±3 minutes to hold peak properties. Similarly, underaging requires tight control of the process variables because of the sharp initial increase of the aging response curve. In the standard age hardening cycle, heating and cooling rates are not critical. However, to assure that aging time does not begin until parts reach temperature, a thermocouple can be placed on the parts to determine when desired temperature has been achieved. The microstructures of Cu-Be alloys in age hardened condition is shown below in Fig.7.17.

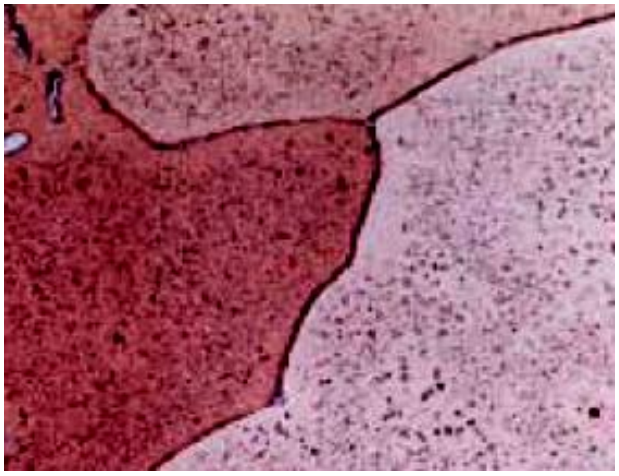
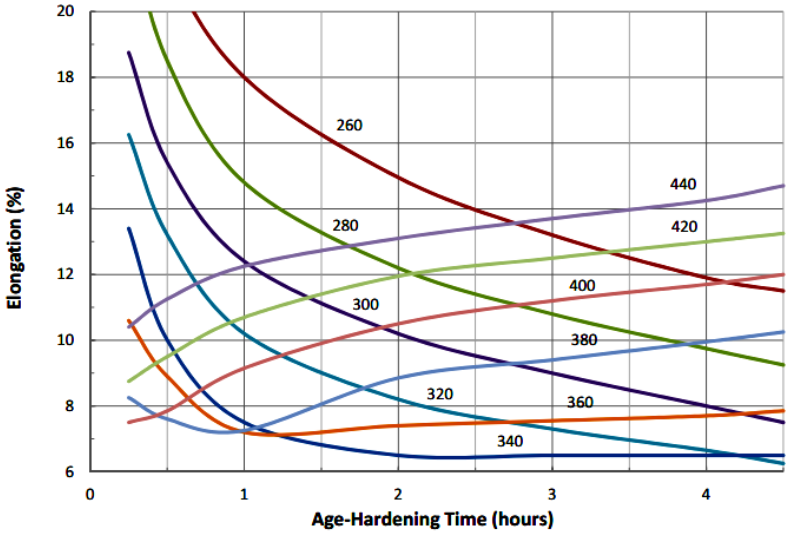
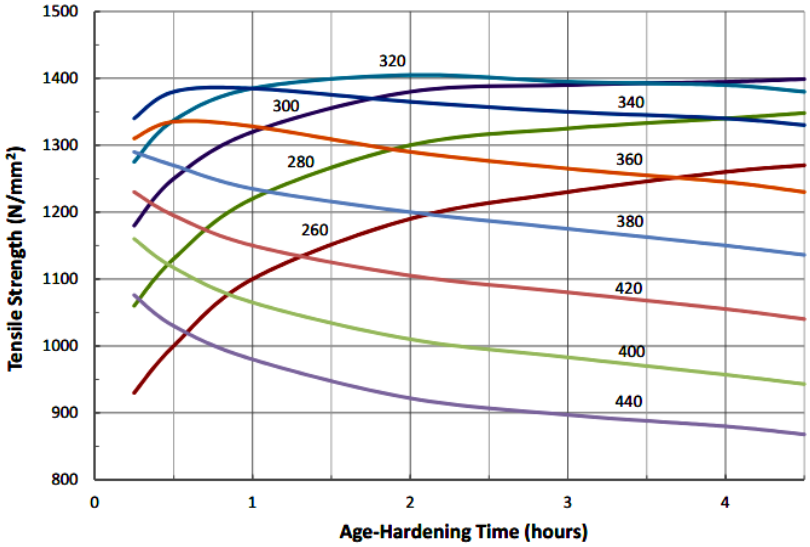


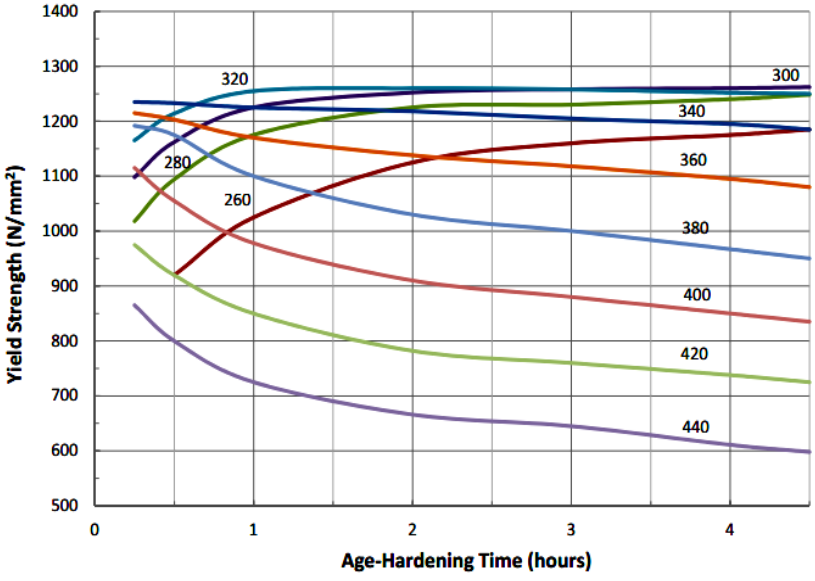
Figure 7.17: Microstructures of Cu-Be alloy after age hardening.

### 7.6.2 PH Design for Cu-Be Alloys

For a certain helical spring application one needs %el along with YS to UTS ratio to be 1.1 for age hardened 25 Cu-Be alloy. Using the following curves suggest a suitable heat treatment schedule.


Elongation (%)
20
18
16
14
12
10
8
6
0
1
2
3
4
Age-Hardening Time (hours)
260
280
300
320
340
360
380
400
420
440


Tensile Strength (N/mm²)
1500
1400
1300
1200
1100
1000
900
800
0
1
2
3
4
Age-Hardening Time (hours)
320
300
280
260
340
360
380
420
400
440


Yield Strength (N/mm²)
1400
1300
1200
1100
1000
900
800
700
600
500
0
1
2
3
4
Age-Hardening Time (hours)
320
300
280
260
340
360
380
400
420
440

### 7.7 Nickel Base Alloys

Nickel base superalloys have an exceptional combination of high temperature strength, toughness and resistance to degradation in corrosive or oxidizing environments. Because of these characteristics they are widely used in aircraft and power generation turbines, rocket engines, nuclear power and chemical processing plants and other challenging environments. The availability of superalloys during past decades has led to a steady increase in the turbine entry temperatures and this trend is expected to continue. New generations of superalloys can tolerate average temperatures of 1050°C with occasional excursions to temperatures as high as 1200°C, which is approximately 90% of the melting point of the material. Increased operating temperatures and higher efficiency in gas turbines and jet engines can reduce $CO_2$ emission, thus contributing to the slowing of climate change. There are various types of nickel base alloys as given Table 7.3.

Table 7.3: Various Ni-base alloys

| Material | Composition | | | | |
|---|---|---|---|---|---|
| | Ni | Fe | Cu | Cr | Mo |
| Nickel 200 | 99.5 | 0.15 | 0.05 | - | - |
| Nickel 201 | 99.5 | 0.15 | 0.05 | - | - |
| Monel 400 | 66.0 | 1.35 | 31.5 | - | - |
| Monel R-405 | 66.0 | 1.35 | 31.5 | - | - |
| Monel K-500 | 65.0 | 1.00 | 29.5 | - | - |
| Inconel 600 | 76.0 | 7.20 | 0.10 | 15.8 | - |
| Inconel 601 | 60.5 | 14.1 | - | 23.0 | - |
| Inconel 617 | 54.0 | - | - | 22.0 | 9.0 |
| Inconel 625 | 61.0 | 2.5 | - | 21.5 | 9.0 |
| Inconel 718 | 52.5 | 18.0 | 0.10 | 19.0 | 3.0 |
| Inconel X-750 | 73.0 | 6.75 | 0.05 | 15.0 | - |
| Hastelloy B | 64.0 | 5.0 | - | - | 28.0 |
| Hastelloy C | 56.0 | 5.5 | - | 15.5 | 16.0 |
| Hastelloy X | 48.0 | 18.5 | - | 22.0 | 9.0 |

#### 7.7.1 Heat Treatment of Nickel and Nickel Alloys

Nickel and nickel alloys may be subjected to one or more of five principal types of heat treatment, depending on chemical composition, fabrication requirements and intended service. These methods include annealing, stress relieve, stress equalizing, solution treating and age hardening. These methods include:

**7.7.1.1 Stress Relieving:** A heat treatment used to remove or reduce stresses in work hardened non-age-hardenable alloys without producing a recrystalized grain structure. Stress relieving temperatures for nickel and nickel alloys from 425 to 870°C, depending on alloy composition and degree of work hardening.

**7.7.1.2 Stress Equalizing:** A low temperature heat treatment used to balance stresses in cold worked material without an appreciable decrease in the mechanical strength produced by cold working.

**7.7.1.3 Age Hardening:** This is only for age hardenable alloys, Table 7.3. For this, at first solution treatment is done at high temperature to put age hardening constituents and carbides into solid solution, normally applied to age hardenable materials before the aging treatment. Then an intermediate temperature aging (425 to 870°C) is done on certain alloys in order to develop maximum strength by precipitation of a dispersed phase throughout the matrix.

**7.7.1.4. Annealing:** As applied to nickel and nickel alloys, annealing consists of heating the metal at a predetermined temperature for a definite time and then slowly or rapidly cooling it, to produce a change in mechanical properties, usually a complete softening as a result of recrystalization. Nickel and nickel alloys that have been hardened by cold working operations, such as rolling, deep drawing, spinning or severe bending, require softening before cold working can be continued. The thermal treatment that will produce this condition is known as annealing or soft annealing. The differences in chemical composition among nickel and nickel alloys necessitate modifications in annealing temperatures as well as in furnace atmospheres. The precipitation hardening alloys must be cooled rapidly after annealing if maximum softness is desired. Three soft annealing methods in general commercial uses are open, closed and salt bath annealing.

**7.7.1.5 Open Annealing:** It is used most often. The material to be annealed is heated at the selected temperature and protected from oxidation by the products of combustion in a fuel heated furnace, or by a reducing gas introduced into an electric furnace. Temperature control is critical because the annealing period is short.

**7.7.1.6 Closed Box Annealing:** This requires more time than open annealing because of the lower temperatures used. Temperature control is less critical than in open annealing. In most instances, the weight of the container exceeds that of the work; consequently, the amount of fuel required, heating time and costs are greater than in open annealing.

**7.7.1.7 Salt Bath Annealing:** It is used for special work with small parts. Inorganic salts, such as chlorides and carbonates of sodium, potassium and barium, which are relatively stable at temperatures considerably above their respective melting points, are fused in large metallic or refractory containers at temperatures up to about 700°C. At higher temperatures, heat resisting Fe-Ni-Cr alloy pots or refractory containers should be used. Excessive fuming of the bath is an indication of its maximum usable temperature. The material to be annealed is placed in molten salts and absorbs heat rapidly. After being annealed, the work metal is quenched in water to free

it from particles of the salt mixture. The annealed material will not be bright and may be flash pickled to achieve a bright surface.

**7.7.1.8 Bright Annealing:** Bright annealing is relatively high temperatures required for soft annealing of nickel and nickel alloys are sufficiently high to cause slight surface oxidation unless the materials are heated in vacuum or in a furnace provided with a reducing atmosphere. Nickel 200, Monel 400 and similar alloys will remain bright and free from discoloration when heated and cooled in a reducing atmosphere. However, nickel alloys containing chromium, titanium and aluminium will form a thin oxide film. Even if oxidation is not important, the furnace atmosphere must be suitably sulfur free and not strongly oxidizing. The protective atmosphere most commonly used in heating nickel and nickel alloys is that provided by controlling the ratio between the fuel and air supplied to burners firing directly into the furnace. A desirable reducing condition may be obtained by using a slight excess of fuel so that the products of combustion contain at least 2% CO plus H (preferably 4%) with no more than 0.05% uncombined oxygen.

**7.7.1.9 Dead Soft Annealing:** When the nickel alloys are annealed at higher temperatures and for longer periods, a condition commonly described as "dead-soft" is obtained and hardness numbers will result that are 10 to 20% lower than those of the "soft" condition. This cannot be accomplished without increasing the grain size of the metal. Therefore, this treatment should be used only for those few applications in which grain size is of little importance.

Among the more important process control factors in annealing nickel and nickel alloys selection of suitably sulfur free fuel for heating, control of furnace temperature, effects of prior cold work and of cooling rates, control of grain size, control of protective atmospheres and protection from contamination by foreign material.

### 7.7.1.10 Age Hardening

Age hardening practices for several nickel alloys are summarized, Table 7.4 below.

Table 7.4: Age hardening practices for Ni-base alloys.

| Alloy | Solution treated | | |
|---|---|---|---|
| | Temperature | Cooling method | Age hardening |
| Monel K-500 | 980 °C | WQ | Heat to 595°C, hold 16h; furnace cool to 540oC, hold 6h; furnace cool to 480°C, hold 8h; air-cool |
| Inconel 718 | 980 °C | AC | Heat to 720°C, hold 8h; furnace cool to 620°C, hold until furnace time for entire age-hardening cycle equals 18h; air cool |
| Inconel X-750 | 1150 °C | AC | Heat to 845°C, hold 24h; air cool; reheat to 705°C, hold 20h; air cool |
| | 980 °C | AC | Heat to 730°C, hold 8h; furnace cool to 620°C, hold until furnace time for entire age-hardening cycle equals 18h; air cool |
| Hastelloy X | 1175 °C | AC | Heat to 760°C, hold 3h; air cool; reheat to 595°C, hold 3h; air cool |

In general nickel alloys are soft when quenched from temperatures ranging from 790 to 1220°C, however, they may be hardened by holding at 480 to 870°C or above and then furnace or air cooling. Quenching is not a prerequisite to aging; the alloys can be hardened from the hot worked and cold worked conditions, as well as from the soft condition. During aging, the precipitation of 'γ', $Ni_3$(AI,Ti) in a high nickel matrix provides significant strengthening to the material. This unique intermetallic phase has a FCC structure similar to that of the matrix and a lattice constant having 1% or less mismatch in the lattice constant with the g matrix. This close matching allows low surface energy and long time stability. Precipitation of γ from the supersaturated matrix yields an increase in strength with increasing precipitation temperature, up to the overaging or coarsening temperature. The amount of γ formed is a function of the hardener content of the alloy. Al, Ti, Nb and Ta are strong γ formers. Effective strengthening by γ decreases above about 0.6Tm as the particles coarsen. The microstructures of fine and coarse precipitates are shown in Fig.7.18.

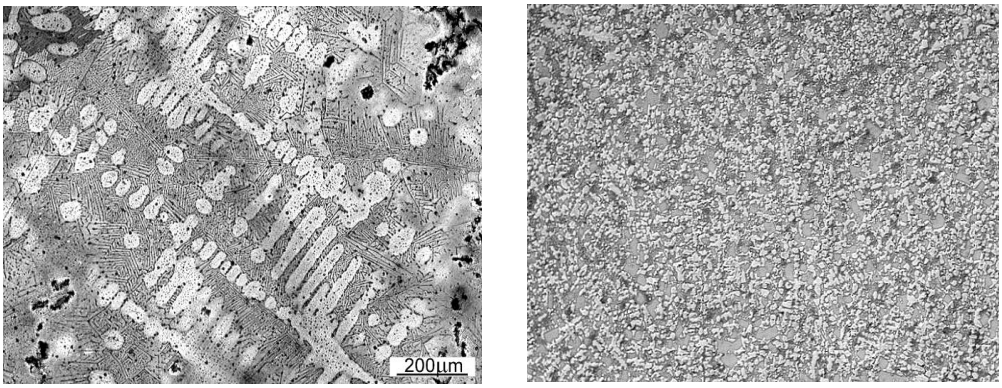



Figure 7.18: Microstructures of Ni base super alloys with fine and coarse precipitates.

**7.8 Heat Treatment of Titanium Alloys**

Titanium and Titanium Alloys are heat treated in order to:

a) Reduce residual stresses developed during fabrication (stress relieving)
b) Produce an optimum combination of ductility, machinability and dimensional and structural stability (annealing)
c) Increase strength (solution treating and aging)
d) Optimize special properties such as fracture toughness, fatigue strength and high temperature creep strength.

Various types of annealing treatments as recrystallization annealing, solution treating and aging treatments, are imposed to achieve selected mechanical properties. Stress relieving and annealing may be employed to prevent preferential chemical attack in some corrosive environments, to prevent distortion (a stabilization treatment) and to condition the metal for subsequent forming and fabricating operations.

### 7.8.1 **Alloy Types and Response to Heat Treatment**

The response of titanium and titanium alloys to heat treatment depends on the composition of the metal and the effects of alloying elements on the α-β crystal transformation of titanium. In addition, not all heat treating cycles are applicable to all titanium alloys, because the various alloys are designed for different purposes some of which are mentioned below.

a) Alloys Ti-5Al-2Sn-2Zr-4Mo-4Cr and Ti-6Al-2Sn-4Zr-6Mo are designed for strength in heavy sections.
b) Alloys Ti-6Al-2Sn-4Zr-2Mo and Ti-6Al-5Zr-0.5Mo-0.2Si for creep resistance.
c) Alloys Ti-6Al-2Nb-1Ta-1Mo and Ti-6Al-4V, for resistance to stress corrosion in aqueous salt solutions and for high fracture toughness.
d) Alloys Ti-5Al-2.5Sn and Ti-2.5Cu for weldability; and
e) Ti-6Al-6V-2Sn, Ti-6Al-4V and Ti-10V-2Fe-3Al for high strength at low-to-moderate temperatures.

Based on the types and amounts of alloying elements they contain, titanium alloys are classified as α, near α, α-β or β alloys. The response of these alloy types to heat treatment is briefly described below in Fig.7.19.

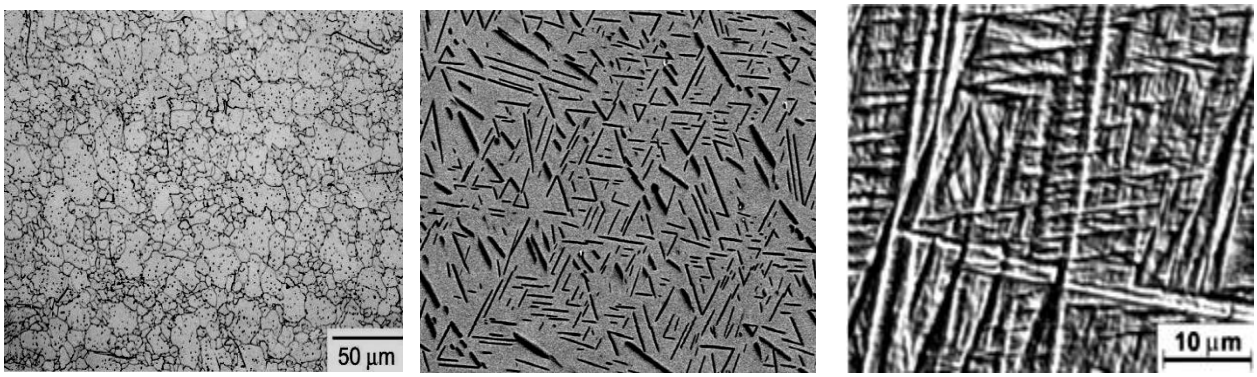



Figure 7.19: Microstructures of alpha, alpha-beta and beta phases of Ti alloys.

Alpha and near alpha titanium alloys can be stress relieved and annealed, but high strength cannot be developed in these alloys by any type of heat treatment (such as aging after a solution beta treatment and quenching). The commercial β alloys are, in reality, metastable β alloys. When these alloys are exposed to selected elevated temperatures, the retained β phase decomposes and strengthening occurs. For β alloys, stress relieving and aging treatments can be combined and annealing and solution treating may be identical operations. Alpha-beta alloys are two phase alloys and as the name suggests, comprise both α and β phases at room temperature. These are the most common and the most versatile of the three types of titanium alloys.

### 7.8.2 Stress Relieving

Titanium and titanium alloys can be stress relieved without adversely affecting strength or ductility. Stress relieving treatments decrease the undesirable residual stresses that result from

first, nonuniform hot forging or deformation from cold forming and straightening, second, asymmetric machining of plate or forgings and third, welding and cooling of castings. The removal of such stresses helps maintain shape stability and eliminates unfavourable conditions, such as the loss of compressive yield strength commonly known as the Bauschinger effect. When symmetrical shapes are machined in the annealed condition using moderate cuts and uniform stock removal, stress relieving may not be required. Compressor disks made of Ti-6Al-4V has been machined satisfactorily in this manner, conforming to dimensional requirements. In contrast, thin rings made of the same alloy could be machined at a higher production rate to more stringent dimensions by stress relieving 2h at 540°C (1000°F) between, rough and final machining. Separate stress relieving may be omitted when the manufacturing sequence can be adjusted to use annealing or hardening as the stress relieving process. For example, forging stresses may be relieved by annealing prior to machining.

### 7.8.3 Annealing

The annealing of titanium and titanium alloys serves primarily to increase fracture toughness, ductility at room temperature, dimensional and thermal stability and creep resistance. Many titanium alloys are placed in service in the annealed state. Because improvement in one or more properties is generally obtained at the expense of some other property, the annealing cycle should be selected according to the objective of the treatment. Common annealing treatments are:

a) Mill annealing
b) Duplex annealing
c) Recrystallization annealing
d) Beta annealing

**7.8.4 Mill annealing** is a general purpose treatment given to all mill products. It is not a full anneal and may leave traces of cold or warm working in the microstructures of heavily worked products, particularly sheet.

**7.8.5 Duplex annealing** alters the shapes, sizes, and distributions of phases to those required for improved creep resistance or fracture toughness. In the duplex anneal of the Corona 5 alloy, for example, the first anneal is near the β transus to globularize the deformed α and to minimize its volume fraction. This is followed by a second, lower-temperature anneal to precipitate new lenticular (acicular) α between the globular α particles. This formation of acicular α is associated with improvements in creep strength and fracture toughness.

**7.8.6 Recrystallization annealing** and β annealing are used to improve fracture toughness. In recrystallization annealing, the alloy is heated into the upper end of the α-β range, held for a

time, and then cooled very slowly. In recent years, recrystallization annealing has replaced β annealing for fracture critical airframe components.

**7.8.7 β (Beta) Annealing** is Like recrystallization annealing, β annealing improves fracture toughness. Beta annealing is done at temperatures above the β transus of the alloy being annealed. To prevent excessive grain growth, the temperature for β annealing should be only slightly higher than the β transus. Annealing times are dependent on section thickness and should be sufficient for complete transformation. Time at temperature after transformation should be held to a minimum to control β grain growth. Larger sections should be fan cooled or water quenched to prevent the formation of a phase at the β grain boundaries. Straightening, sizing, and flattening of titanium alloys are often necessary in order to meet dimensional requirements. The straightening of bar to close tolerances and the flattening of sheet present major problems for titanium producers and fabricators.

**7.8.8 Solution Treating and Aging**

A wide range of strength levels can be obtained in α-β or β alloys by solution treating and aging. The origin of heat-treating responses of titanium alloys lies in the instability of the high temperature β phase at lower temperatures. Heating of an α-β alloy to the solution treating temperature produces a higher ratio of β phase. This partitioning of phases is maintained by quenching; on subsequent aging, decomposition of the unstable β phase occurs, providing high strength. Commercial β alloys generally supplied in the solution-treated condition, and need only to be aged. Solution treating of titanium alloys generally involves heating to temperatures either slightly above or slightly below the β transition temperature. The solution treating temperature selected depends on the alloy type and practical considerations briefly described below.

β (Beta) alloys are normally obtained from producers in the solution-treated condition. If reheating is required, soak times should be only as long as necessary to obtain complete solutioning. Solution-treating temperatures for β alloys are above the β transus; because no second phase is present, grain growth can proceed rapidly.

α-β (Alpha-beta) alloys. Selection of a solution treatment temperature for α-β alloys is based on the combination of mechanical properties desired after aging. A change in the solution-treating temperature of α-β alloys alters the amounts of β phase and consequently changes the response to aging.

To obtain high strength with adequate ductility, it is necessary to solution treat at a temperature high in the α-β field, normally 25 to 85°C (50 to 150°F) below the β transus of the alloy. If high fracture toughness or improved resistance to stress corrosion is required, β annealing or β solution treating may be desirable. However, heat treating α-β alloys in the β range causes a significant loss in ductility. These alloys are usually solution heat treated below the β transus to

obtain an optimum balance of ductility, fracture toughness, creep, and stress rupture properties. After being cleaned, titanium components should be loaded into fixtures or racks that will permit free access to the heating and quenching media. Thick and thin components of the same alloy may be solution treated together, but the time at temperature is determined by the thickness of the section.

### 7.8.9 Alloy Design for Age Hardenable of Ti Base Alloys

It has been mentioned that for age hardening of titanium base alloy, the phase must be in the metastable beta or alpha + metastable beta phase. In the case of stable beta phase age hardening will be not possible, i.e. this phase will remain unchanged at or below room temperature, Fig.7.20.

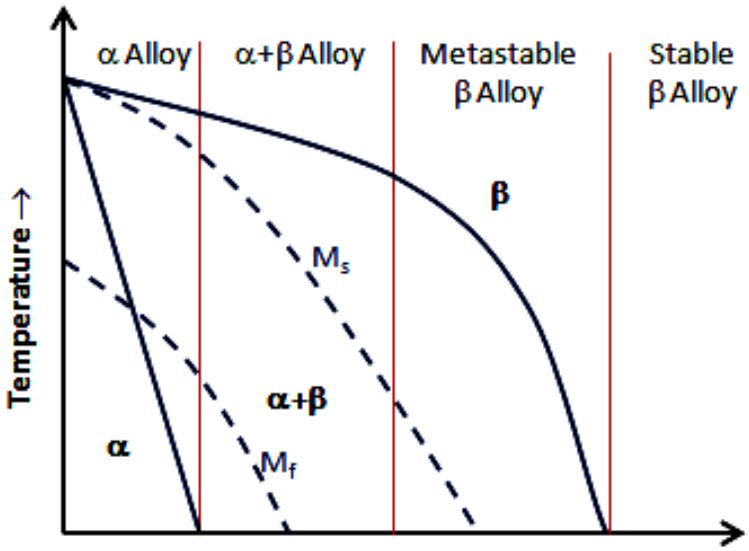



Figure 7.20: Effects of cooling rates on microstructures of Ti alloys.

The stability of beta phase depends on alloy content. The overall effects of alloying elements could be guessed by Mo equivalent from less complex and simplified Ti alloy:

$$[Mo]_{eq} = [Mo] + 0.67\,[V] + 2.9\,[Fe] + 1.6\,[Cr]$$

The single beta phase will be stabilized if ambient temperature if the case satisfies the following condition: Mo eq. > 10.